# Supplementary Information: Organics on oxidic metal surfaces: A first-principles DFT study of PMDA and ODA fragments on the pristine and mildly oxidized surfaces of Cu(111)

Jong-Hun Park,* Ji-Hwan Lee,* and Aloysius Soon†

*Global $E^3$ Institute and Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

(Dated: June 24, 2016)

* These authors contributed equally to this work.

† Corresponding author. E-mail: aloysius.soon@yonsei.ac.kr

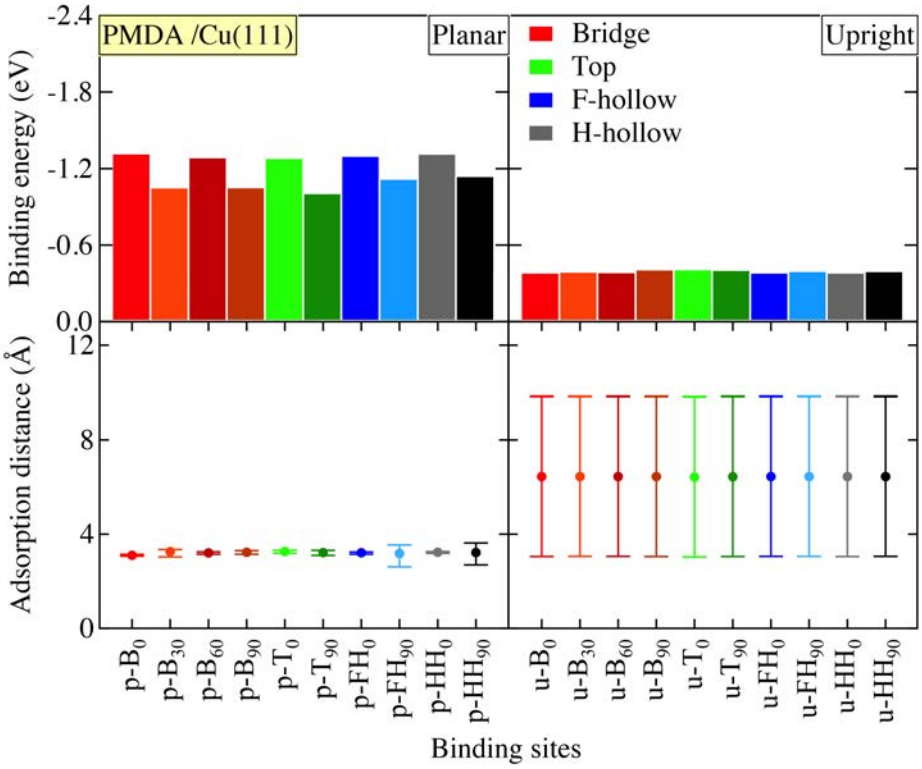


FIG. S1. (Color online) For PMDA/Cu(111), calculated binding energies (up) and optimized adsorption distances (down) with planar configuration (left) and upright configuration (right). Upper and lower bars indicate the maximum and the minimum distances from surface to atoms in molecule and middle dots mean the average adsorption distances. The binding energy and optimized adsorption distance for all considered adsorption configurations are demonstrated. "p" and "u" in the bottom axis indicate planar and upright configurations of PMDA molecule. "B", "T", "FH", and "HH" indicate bridge (B), top (T), FCC-hollow (FH), and HCP-hollow (HH) sites, respectively. The numbers subscripted in the bottom axis demonstrate the degree of the rotation of molecule on surfaces. Since top and hollow sites have 3-fold symmetry, 0 ° and 90 ° rotations are considered for the sites.

TABLE S1. For PMDA/Cu(111), calculated binding energies and optimized adsorption distances with planar configuration and upright configuration. $d_{\max}$ and $d_{\min}$ indicate the maximum and the minimum distances from the surface to atoms in molecule and $\bar{d}$ means the average adsorption distance. The binding energy and optimized adsorption distance for all considered configurations are demonstrated and corresponding to Fig. S1 in supplementary information.

| Configuration | Sites | $E_{\mathrm{b}}$ (eV/unit) | $d_{\max}$ (Å) | $\bar{d}$ (Å) | $d_{\min}$ (Å) |
|---|---|---|---|---|---|
| Planar | $B_0$ | −1.33 | 3.139 | 3.104 | 3.062 |
| | $B_{30}$ | −1.06 | 3.352 | 3.253 | 3.030 |
| | $B_{60}$ | −1.29 | 3.248 | 3.206 | 3.149 |
| | $B_{90}$ | −1.06 | 3.301 | 3.228 | 3.145 |
| | $T_0$ | −1.29 | 3.321 | 3.263 | 3.188 |
| | $T_{90}$ | −1.01 | 3.314 | 3.213 | 3.094 |
| | $FH_0$ | −1.31 | 3.243 | 3.207 | 3.149 |
| | $FH_{90}$ | −1.13 | 3.543 | 3.179 | 2.610 |
| | $HH_0$ | −1.32 | 3.263 | 3.232 | 3.186 |
| | $HH_{90}$ | −1.15 | 3.623 | 3.216 | 2.697 |
| Upright | $B_0$ | −0.39 | 9.841 | 6.444 | 3.053 |
| | $B_{30}$ | −0.40 | 9.842 | 6.446 | 3.056 |
| | $B_{60}$ | −0.39 | 9.842 | 6.446 | 3.055 |
| | $B_{90}$ | −0.41 | 9.841 | 6.444 | 3.053 |
| | $T_0$ | −0.42 | 9.821 | 6.424 | 3.032 |
| | $T_{90}$ | −0.41 | 9.838 | 6.442 | 3.049 |
| | $FH_0$ | −0.39 | 9.842 | 6.446 | 3.055 |
| | $FH_{90}$ | −0.40 | 9.842 | 6.446 | 3.056 |
| | $HH_0$ | −0.39 | 9.840 | 6.444 | 3.052 |
| | $HH_{90}$ | −0.40 | 9.841 | 6.445 | 3.055 |

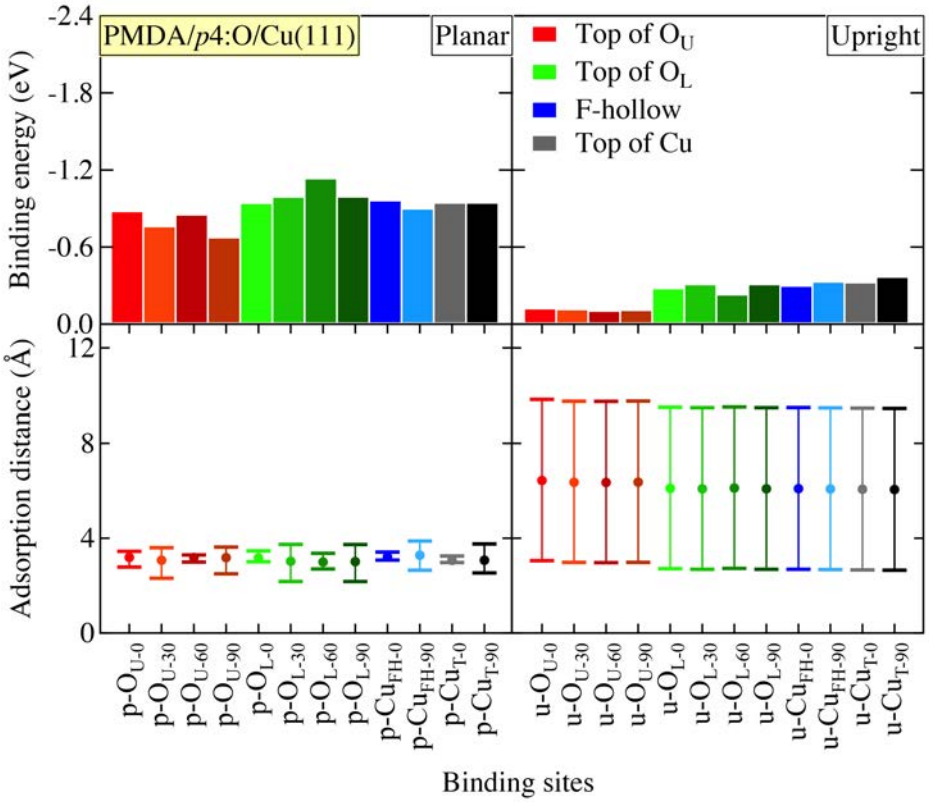


FIG. S2. (Color online) For PMDA/$p4$:O/Cu(111), calculated binding energies (up) and optimized adsorption distances (down) with planar configuration (left) and upright configuration (right). Upper and lower bars indicate the maximum and the minimum distances from the surface to atoms in molecule and middle dots mean the average adsorption distances. The binding energies and optimized adsorption distances for all considered adsorption configurations are demonstrated. "p" and "u" in the bottom axis indicate planar and upright configurations of PMDA molecule. "$O_U$", "$O_L$", "$Cu_{FH}$", and "$Cu_T$" indicate atop of oxygen upper (U) and lower (L) sites on the surface oxide layer, FCC-hollow (FH) and atop (T) sites of Cu in the middle of honeycomb shape of surface oxide ring in the $p4$:O surface, respectively. The numbers subscripted in the bottom axis demonstrate the degree of the rotation of molecule on surfaces. Since $Cu_{FH}$ and $Cu_T$ sites have 3-fold symmetry, 0 ° and 90 ° rotations are considered for the sites.

TABLE S2. For PMDA/$p4$:O/Cu(111), calculated binding energies and optimized adsorption distances with planar configuration and upright configuration. $d_{\max}$ and $d_{\min}$ indicate the maximum and the minimum distances from the surface to atoms in molecule and $\bar{d}$ means the average adsorption distance. The binding energy and optimized adsorption distances for all considered configurations are demonstrated and corresponding to Fig. S2 in supplementary information.

| Configuration | Sites | $E_{\mathrm{b}}$ (eV/unit) | $d_{\max}$ (Å) | $\bar{d}$ (Å) | $d_{\min}$ (Å) |
|---|---|---|---|---|---|
| Planar | $O_{\text{U-0}}$ | −0.88 | 3.449 | 3.189 | 2.781 |
| | $O_{\text{U-30}}$ | −0.77 | 3.598 | 3.072 | 2.310 |
| | $O_{\text{U-60}}$ | −0.86 | 3.294 | 3.188 | 2.994 |
| | $O_{\text{U-90}}$ | −0.68 | 3.624 | 3.181 | 2.496 |
| | $O_{\text{L-0}}$ | −0.95 | 3.467 | 3.170 | 3.005 |
| | $O_{\text{L-30}}$ | −1.00 | 3.741 | 3.026 | 2.171 |
| | $O_{\text{L-60}}$ | −1.14 | 3.365 | 2.994 | 2.703 |
| | $O_{\text{L-90}}$ | −1.00 | 3.731 | 3.016 | 2.175 |
| | $Cu_{\text{FH-0}}$ | −0.97 | 3.416 | 3.208 | 3.077 |
| | $Cu_{\text{FH-90}}$ | −0.91 | 3.876 | 3.282 | 2.648 |
| | $Cu_{\text{T-0}}$ | −0.95 | 3.250 | 3.062 | 2.971 |
| | $Cu_{\text{T-90}}$ | −0.95 | 3.758 | 3.073 | 2.536 |
| Upright | $O_{\text{U-0}}$ | −0.13 | 9.828 | 6.431 | 3.050 |
| | $O_{\text{U-30}}$ | −0.12 | 9.754 | 6.359 | 2.979 |
| | $O_{\text{U-60}}$ | −0.11 | 9.744 | 6.348 | 2.969 |
| | $O_{\text{U-90}}$ | −0.12 | 9.758 | 6.363 | 2.982 |
| | $O_{\text{L-0}}$ | −0.28 | 9.498 | 6.102 | 2.712 |
| | $O_{\text{L-30}}$ | −0.32 | 9.476 | 6.080 | 2.690 |
| | $O_{\text{L-60}}$ | −0.24 | 9.509 | 6.115 | 2.724 |
| | $O_{\text{L-90}}$ | −0.32 | 9.477 | 6.081 | 2.691 |
| | $Cu_{\text{FH-0}}$ | −0.30 | 9.482 | 6.086 | 2.689 |
| | $Cu_{\text{FH-90}}$ | −0.34 | 9.472 | 6.076 | 2.678 |
| | $Cu_{\text{T-0}}$ | −0.33 | 9.459 | 6.062 | 2.664 |
| | $Cu_{\text{T-90}}$ | −0.37 | 9.447 | 6.049 | 2.651 |

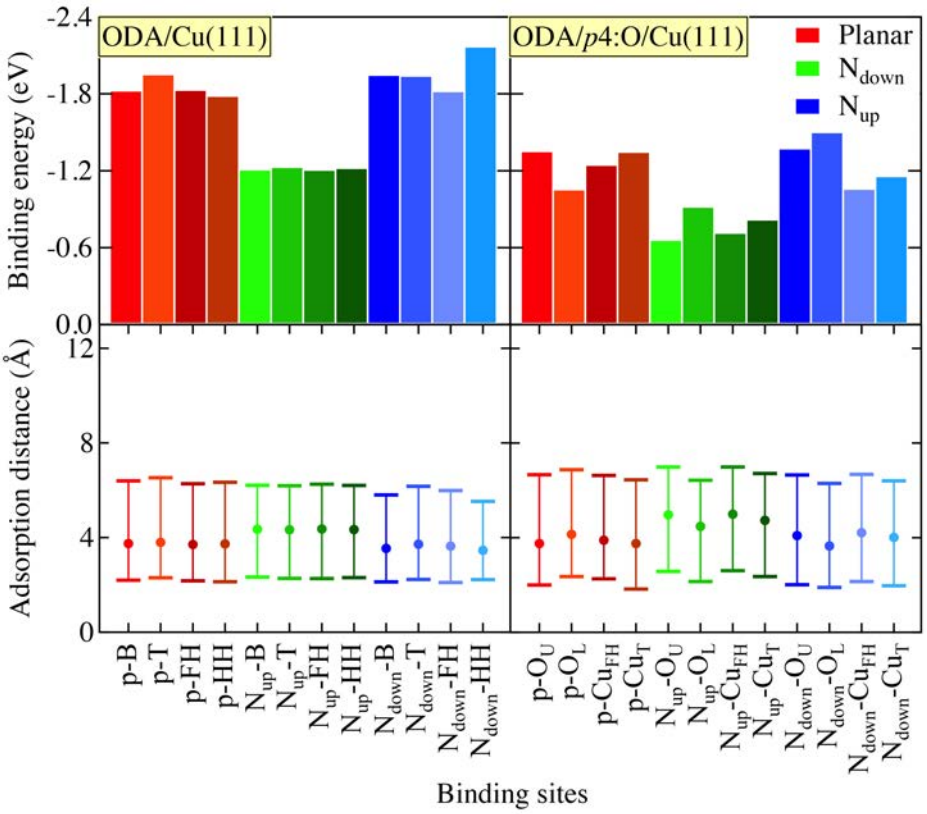


FIG. S3. (Color online) For ODA adsorption, calculated binding energies (up) and optimized adsorption distances (down) on Cu(111) (left) and $p4$:O/Cu(111) (right). Upper and lower bars indicate the maximum and the minimum distances from the surface to atoms in molecule and middle dot means the average adsorption distance. The binding energy and optimized adsorption distance for all considered configurations are demonstrated. "p", "$N_{up}$", and "$N_{down}$" in the bottom axis indicate planar and nitrogen up and down configuration of ODA molecule. In ODA/Cu(111) case, "B", "T", "FH", and "HH" indicate bridge (B), top (T), FCC-hollow (FH), and HCP-hollow (HH) sites, respectively. In ODA/$p4$:O/Cu(111) case, "$O_U$", "$O_L$", "$Cu_{FH}$", and "$Cu_T$" indicate atop of oxygen upper (U) and lower (L) sites on the surface oxide layer, FCC-hollow (FH) and atop (T) sites of Cu in the middle of honeycomb shape of surface oxide ring in the $p4$:O surface, respectively.

TABLE S3. For ODA/Cu(111), calculated binding energies and optimized adsorption distances with planar configuration and upright configuration. $d_{\max}$ and $d_{\min}$ indicate the maximum and the minimum distances from the surface to atoms in molecule and $\bar{d}$ means the average adsorption distance. The binding energy and optimized adsorption distance for all considered configurations are demonstrated and corresponding to Fig. S3 in supplementary information. "B", "T", "FH", and "HH" indicate bridge (B), top (T), FCC-hollow (FH), and HCP-hollow (HH) sites, respectively.

| Configuration | Sites | $E_{\mathrm{b}}$ (eV/unit) | $d_{\max}$ (Å) | $\bar{d}$ (Å) | $d_{\min}$ (Å) |
|---|---|---|---|---|---|
| Planar | B | −1.83 | 6.39 | 3.74 | 2.20 |
| | T | −1.96 | 6.53 | 3.80 | 2.30 |
| | FH | −1.84 | 6.27 | 3.71 | 2.17 |
| | HH | −1.79 | 6.34 | 3.73 | 2.14 |
| $N_{up}$ | B | −1.22 | 6.21 | 4.35 | 2.33 |
| | T | −1.24 | 6.19 | 4.33 | 2.27 |
| | FH | −1.21 | 6.25 | 4.36 | 2.27 |
| | HH | −1.23 | 6.20 | 4.34 | 2.31 |
| $N_{down}$ | B | −1.95 | 5.80 | 3.54 | 2.13 |
| | T | −1.95 | 6.17 | 3.72 | 2.23 |
| | FH | −1.83 | 5.99 | 3.64 | 2.10 |
| | HH | −2.17 | 5.53 | 3.46 | 2.22 |

TABLE S4. For ODA/$p4$:O/Cu(111),calculated binding energies and optimized adsorption distances with planar configuration and upright configuration. $d_{\max}$ and $d_{\min}$ indicate the maximum and the minimum distances from the surface to atoms in molecule and $\bar{d}$ means the average adsorption distance. The binding energy and optimized adsorption distance for all considered configurations are demonstrated and corresponding to Fig. S3 in supplementary information. "$O_U$", "$O_L$", "$Cu_{FH}$", and "$Cu_T$" indicate atop of oxygen upper (U) and lower (L) sites on the surface oxide layer, FCC-hollow (FH) and atop (T) sites of Cu in the middle of honeycomb shape of surface oxide ring in the $p4$:O surface, respectively.

| Configuration | Sites | $E_{\mathrm{b}}$ (eV/unit) | $d_{\max}$ (Å) | $\bar{d}$ (Å) | $d_{\min}$ (Å) |
|---|---|---|---|---|---|
| Planar | $O_U$ | −1.36 | 6.66 | 3.75 | 2.00 |
| | $O_L$ | −1.06 | 6.87 | 4.14 | 2.35 |
| | $Cu_{FH}$ | −1.25 | 6.63 | 3.89 | 2.26 |
| | $Cu_T$ | −1.35 | 6.45 | 3.75 | 1.83 |
| $N_{up}$ | $O_U$ | −0.67 | 6.99 | 4.97 | 2.57 |
| | $O_L$ | −0.93 | 6.43 | 4.48 | 2.15 |
| | $Cu_{FH}$ | −0.72 | 6.98 | 4.99 | 2.60 |
| | $Cu_T$ | −0.83 | 6.71 | 4.73 | 2.35 |
| $N_{down}$ | $O_U$ | −1.38 | 6.65 | 4.09 | 2.01 |
| | $O_L$ | −1.51 | 6.29 | 3.65 | 1.90 |
| | $Cu_{FH}$ | −1.07 | 6.68 | 4.21 | 2.15 |
| | $Cu_T$ | −1.16 | 6.40 | 4.02 | 1.97 |

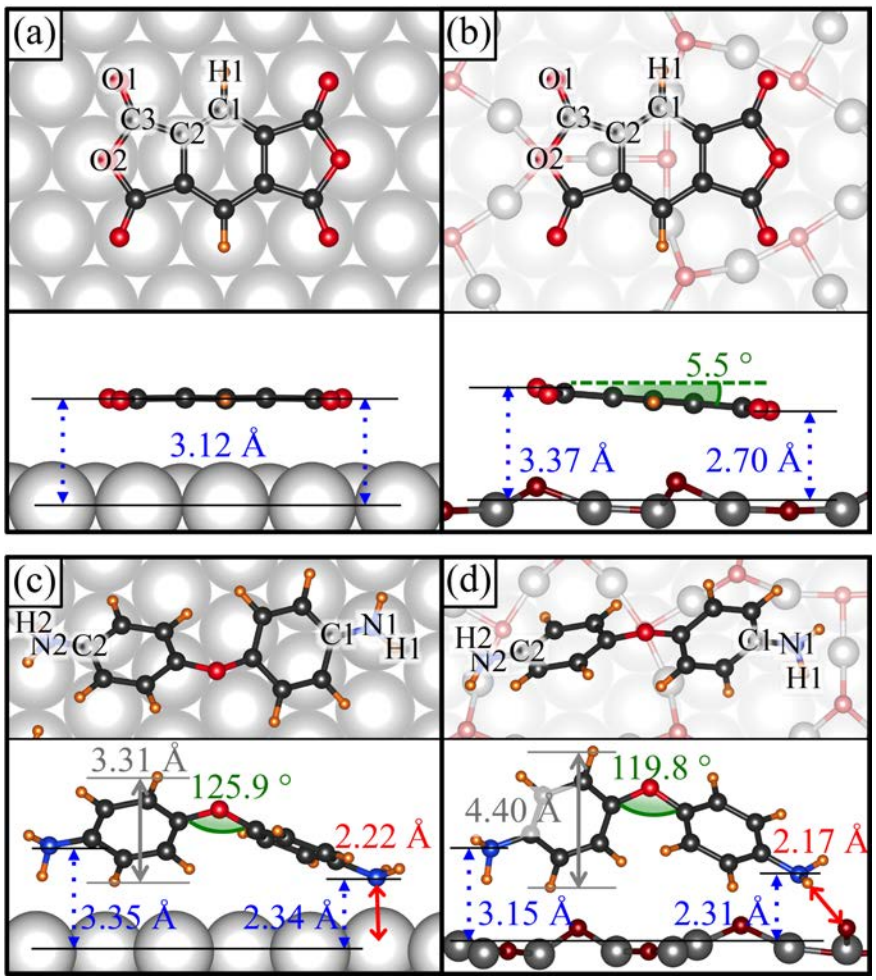


FIG. S4. (Color online) In (a) and (c), the most stable adsorption structures of PMDA and ODA on Cu(111), and in (b) and (d), those of $p4$:O/Cu(111) are shown. Blue, red, and grey arrows are molecule to surface distance, bond distance N-Cu in (c) and NH$\cdots$O in (d), and molecular thickness. Green fan-shapes are molecular tilting angle from parallel to the surface in (b) and C-O-C angles in (c) and (d). Here, we name the atoms with numbers in the molecule due to compare the change of intramolecular bond distances before and after adsorption. Tab. S5 and S6 show the intramolecular bond distances and changes in the most stable adsorption structures.

TABLE S5. The averaged (up) and specific intramolecular bond (down) length (Å) in PMDA molecule for gaseous molecule, PMDA/Cu(111), and PMDA/$p4$:O/Cu(111) and the bond length change (%) for PMDA/Cu(111) and PMDA/$p4$:O/Cu(111). The numbers in the brackets for the bonds indicate the numbers of the bond in PMDA molecule. 10 C-C bonds exist in PMDA molecule and 6 bonds are in the benzene ring (C-C benzene) and 4 bonds are out of the benzene ring with single bond (C-C single). 8 C-O bonds are present and 4 single bonds (C-O single) and 4 carbonyl group like double bonds (C-O double) exist. The specific intramolecular bond distances are demonstrated in the bottom side and the location of the specific atoms are shown in Fig. S4.

| Bond | PMDA | PMDA/Cu(111) | | PMDA/$p4$:O/Cu(111) | |
|---|---|---|---|---|---|
| | $d_{\mathrm{bond}}$ (Å) | $d_{\mathrm{bond}}$ (Å) | $\Delta d_{\mathrm{bond}}$ (%) | $d_{\mathrm{bond}}$ (Å) | $\Delta d_{\mathrm{bond}}$ (%) |
| C-C(10) | 1.433 | 1.429 | −0.2 | 1.434 | 0.1 |
| C-C benzene(6) | 1.396 | 1.396 | 0.0 | 1.398 | 0.1 |
| C-C single(4) | 1.487 | 1.478 | −0.6 | 1.487 | 0.0 |
| C-H(2) | 1.090 | 1.090 | 0.1 | 1.090 | 0.0 |
| C-O(8) | 1.308 | 1.311 | 0.3 | 1.308 | 0.0 |
| C-O single(4) | 1.411 | 1.413 | 0.1 | 1.410 | −0.1 |
| C-O double(4) | 1.204 | 1.210 | 0.4 | 1.206 | 0.1 |
| C1-C2 | 1.393 | 1.393 | 0.0 | 1.397 | 0.3 |
| C2-C3 | 1.487 | 1.479 | −0.5 | 1.488 | 0.1 |
| O1-C3 | 1.204 | 1.210 | 0.4 | 1.206 | 0.1 |
| O2-C3 | 1.410 | 1.412 | 0.2 | 1.408 | −0.2 |
| H1-C1 | 1.090 | 1.090 | 0.0 | 1.090 | 0.0 |

TABLE S6. The averaged (up) and specific intramolecular bond (down) length (Å) in ODA molecule for gaseous molecule, ODA/Cu(111), and ODA/$p4$:O/Cu(111) and the bond length change (%) for ODA/Cu(111) and ODA/$p4$:O/Cu(111). The numbers in the brackets for the bonds indicate the numbers of the bond in ODA molecule. The specific intramolecular bond distances are demonstrated in the bottom side and the location of the specific atoms are shown in Fig. S4.

| Bond | ODA | ODA/Cu(111) | | ODA/$p4$:O/Cu(111) | |
|---|---|---|---|---|---|
| | $d_{\mathrm{bond}}$ (Å) | $d_{\mathrm{bond}}$ (Å) | $\Delta d_{\mathrm{bond}}$ (%) | $d_{\mathrm{bond}}$ (Å) | $\Delta d_{\mathrm{bond}}$ (%) |
| C-C(12) | 1.399 | 1.400 | 0.0 | 1.399 | 0.0 |
| C-H(8) | 1.091 | 1.091 | 0.0 | 1.091 | 0.0 |
| C-O(2) | 1.387 | 1.385 | −0.1 | 1.387 | 0.0 |
| C-N(2) | 1.402 | 1.412 | 0.7 | 1.396 | −0.5 |
| N-H(4) | 1.015 | 1.021 | 0.6 | 1.018 | 0.3 |
| N1-C1 | 1.402 | 1.426 | 1.7 | 1.402 | 0.0 |
| N1-H1 | 1.015 | 1.020 | 0.5 | 1.022 | 0.6 |
| N2-C2 | 1.402 | 1.397 | −0.3 | 1.389 | −0.9 |
| N2-H2 | 1.015 | 1.025 | 1.0 | 1.017 | 0.2 |

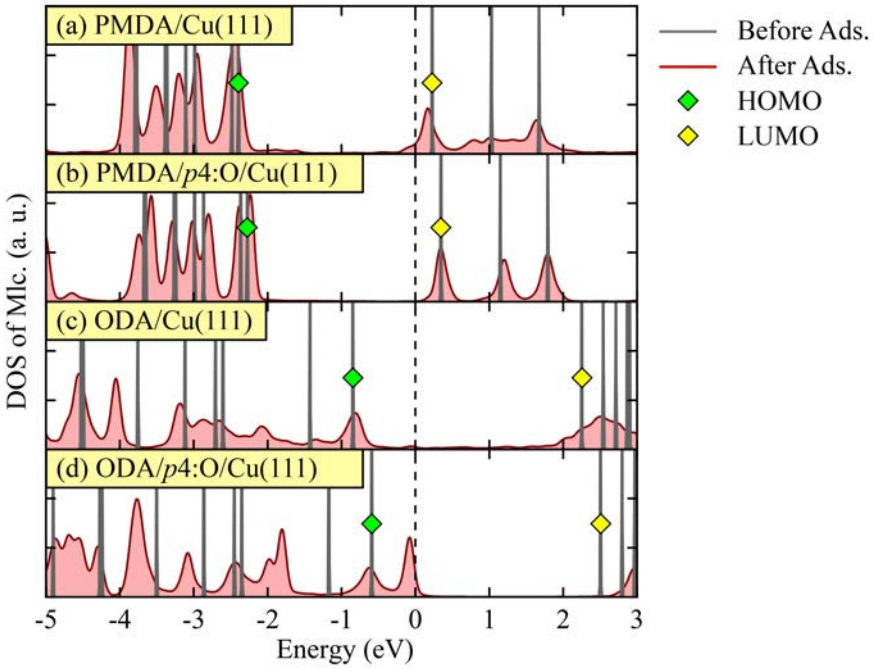


FIG. S5. (Color online) The total DOS of molecules before and after adsorption in each system. Grey and red lines are the molecular energy states before and after the adsorption. Green and yellow diamond shapes indicate the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The molecular states are broadened in both PMDA and ODA cases. However, the broadening in the ODA adsorption cases are more significant than in the PMDA adsorption cases.