

## Supplementary Information

### **Investigation of Amperometric Sensing Mechanism in Gold-C<sub>60</sub>-Gold Molecular Dot**

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## Au-C<sub>60</sub> Molecular Dot Density Of States

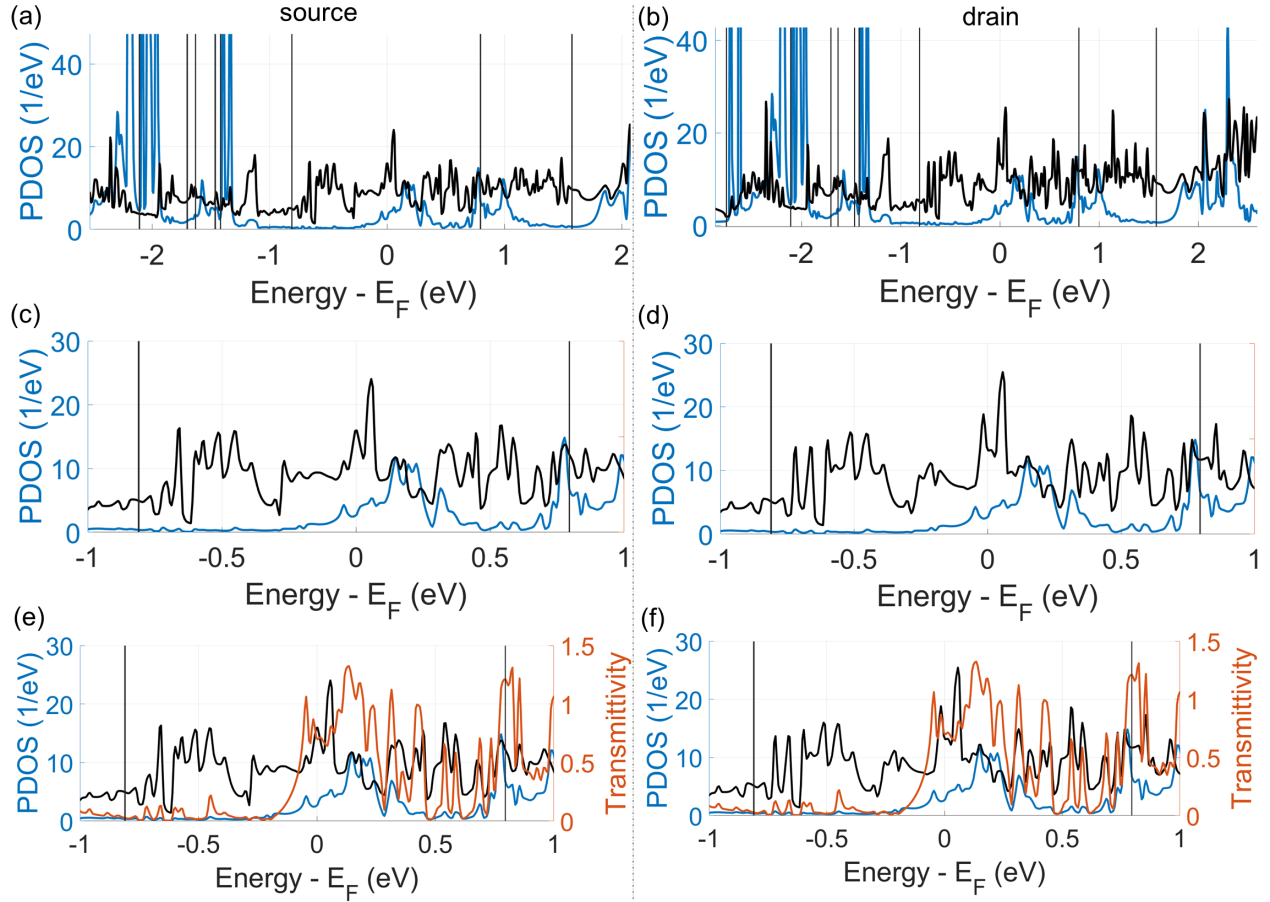


Figure S1: (a) Equilibrium PDOS (blue) onto the C<sub>60</sub> molecular channel and PDOS (black) onto the source electrode, the vertical lines are the isolated C<sub>60</sub> energy levels; (b) equilibrium PDOS (blue) onto the C<sub>60</sub> molecular channel and PDOS (black) onto the drain electrode, the vertical lines are the isolated C<sub>60</sub> energy levels; (c) enlargement of (a) for energies in the range -1 eV ÷ +1 eV; (d) enlargement of (b) for energies in the range -1 eV ÷ +1 eV; (e) equilibrium PDOS (blue) onto the C<sub>60</sub> molecular channel, PDOS (black) onto the source electrode and equilibrium *TS* (orange); (f) equilibrium PDOS (blue) onto the C<sub>60</sub> molecular channel, PDOS (black) onto the drain electrode and equilibrium *TS* (orange).

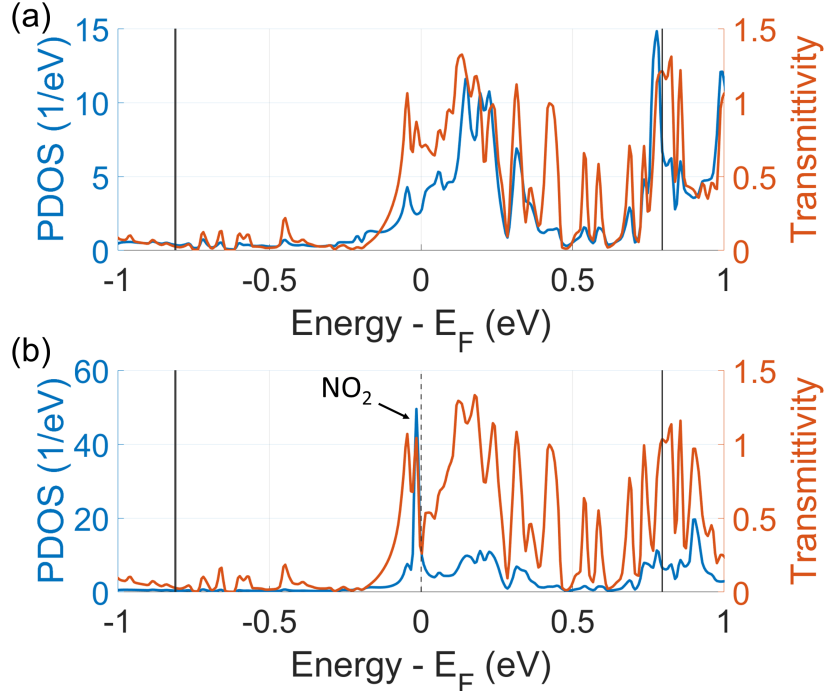


Figure S2: (a) Equilibrium PDOS (blue) onto the C<sub>60</sub> molecular channel and relative  $TS$  (orange) of the Au-C<sub>60</sub> molecular dot. Vertical lines are the isolated C<sub>60</sub> energy levels in the considered energy range. (b) Equilibrium PDOS (blue) onto the C<sub>60</sub> and NO<sub>2</sub> molecules and relative  $TS$  (orange). Solid vertical lines are the isolated C<sub>60</sub> energy levels in the considered energy range while the dashed one is an NO<sub>2</sub> energy level present within the considered energy range.

## Interaction Energy

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We calculate the C<sub>60</sub>-target interaction energies in QuantumATK [1] through DFT method, employing the Generalized Gradient Approximation (GGA), with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional, polarized double- $\zeta$  (DZP) basis set, van der Waals (vdW) correction Grimme DFT-D3 [2]. We enable the Counter-Poise (CP) correction scheme for the Basis Set Superposition Error (BSSE), and we use the parallel conjugate gradient Poisson solver with Dirichlet boundary conditions in all directions. Convergence is achieved at the  $10^{-5}$  tolerance over the total energy, with Pulay mixing scheme over the Hamiltonian variable. We calculate the interaction energy from its definition, as follows:

$$E_{interaction} = E_{[C60+target]} - (E_{[C60]} + E_{[target]}) \quad (1)$$

Chemical Species / Targets	$E_{interaction}$ (kJ/mol)
Ar	223.6
C <sub>4</sub> H <sub>10</sub>	-5.46
CH <sub>4</sub>	21.14
CO <sub>2</sub>	122.36
CO	156.52
H <sub>2</sub> O (flat)	65.12
H <sub>2</sub> O (H down)	-1.51
H <sub>2</sub> O (O down)	68.2
N <sub>2</sub>	177
NH <sub>3</sub> (H down)	186.1
NH <sub>3</sub> (N down)	188.9
NO (flat)	127.8
NO (N down)	83.43
NO (O down)	73.3
NO <sub>2</sub> (flat)	122
NO <sub>2</sub> (N down)	32.81
NO <sub>2</sub> (O down)	90.51
O <sub>2</sub>	111.77

Table S3: Interaction energies for the considered targets and common atmospheric compounds.

## References

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- [1] S. Smidstrup, T. Markussen, P. Vancraeyveld, J. Wellendorff, J. Schneider, T. Gunst, B. Verstichel, D. Stradi, U. Martinez, A. Blom, M. Brandbyge, and K. Stokbro, "QuantumATK: an integrated platform of electronic and atomic-scale modelling tools," *Journal of Physics: Condensed Matter*, vol. 32, no. 1, p. 015901, oct 2019.
- [2] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, "A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements h-pu," *The Journal of Chemical Physics*, vol. 132, no. 15, p. 154104, 2010.