

Supporting Information:  
Hubbard NEGF Analysis of Photocurrent in  
Nitroazobenzene Molecular Junction

Kuniyuki Miwa,<sup>†</sup> Amin Morteza Najarian,<sup>‡</sup> Richard L. McCreery,<sup>‡</sup> and Michael  
Galperin<sup>\*,†</sup>

<sup>†</sup>*Department of Chemistry and Biochemistry, University of California San Diego, La Jolla,  
CA 92034, USA*

<sup>‡</sup>*Department of Chemistry, University of Alberta, Edmonton, Canada*

E-mail: [migalperin@ucsd.edu](mailto:migalperin@ucsd.edu)

Phone: +1-858-246-0511

## List of symbols

- NEGF - nonequilibrium Green's function
- DFT - density functional theory
- TDDFT - time-dependent DFT
- $M$  - molecule
- $B (L, R, rad)$  - bath (left contact, right contact, radiation field)
- $S$  - molecular many-body state
- $ET$  - electron transfer transition (electron transition between molecule and contacts)
- $OT$  - optical transfer transition (intra-molecular electron transfer)

# First principles simulations

Density functional theory (DFT) and time-dependent DFT (TDDFT) of electronic structure of isolated nitroazobenzene molecule were performed with the Gaussian 16 program package.<sup>1</sup> Wavefunctions were expanded with the triple-zeta valence basis set with polarization and diffuse functions (6-311++G(2d,2p)) on all atoms and the hybrid B3LYP functional was used for all calculations of electronic structure reported in the letter.

A geometry for the ground electronic state of the neutral molecule was optimized, and vibrational frequencies for the optimized geometry were analyzed to confirm that all positive frequencies were obtained.

The vertical electron attachment/detachment energies were estimated from the difference between total energies for different charge states of the molecule. In particular, the electron attachment energy was estimated as difference between energies of neutral molecule and cation in their ground states. Its value, 8.75 eV, is close to the one obtained by ultraviolet photoelectron spectroscopy (UPS) experiment.<sup>2</sup> The electron detachment energy was given by energy difference between neutral molecule and anion in their ground states, its value was 1.94 eV. Table S1 gives energies of neutral, cation and anion ground states of the molecule.

Table S1: Energies of ground states (eV)

$E_{N_g}$	$E_{A_g}$	$E_{C_g}$
-21156.7710	-21158.7146	-21148.0182

The vertical excitation energies and transition dipole moments were investigated with the aid of TDDFT calculations at the B3LYP/6-311++(2d,2p) level. Among electronic excitations, we consider only excitation of 3.42 eV. This excitation demonstrates the largest oscillator strength  $f = 0.836$ . Figure S1 sketches electronic and optical transitions considered in the simulations. Table S2 shows several lowest excitation transitions and their oscillator strengths.

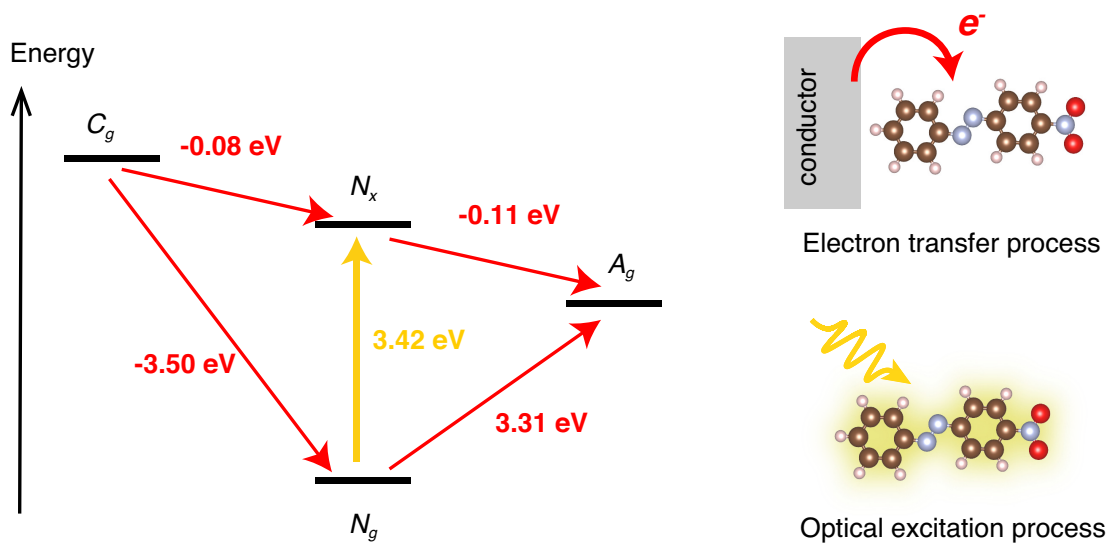


Figure S1: Sketch of electron (red line) and optical (yellow line) transitions considered in the simulations.

Table S2: Optical transitions in neutral molecule

#	Excitation energy (eV)	Oscillator strength
1	2.3933	0.0000
2	3.4214	0.8356
3	3.6539	0.0000
4	3.6966	0.0436
5	3.8765	0.0001
6	3.9243	0.0221
7	4.1810	0.0002
8	4.3327	0.0778
9	4.6369	0.0184

## Choice of parameters

Parameters for coupling of molecule to contacts and for electron transfer between molecule units are fitting parameters. They are chosen in a physically reasonable range to reproduce experimental data.

Regarding choice of escape rates, we note that, the TDDFT calculations of NAB indicate that orbitals responsible for optical transitions are HOMO-1 and LUMO (HOMO-LUMO transition has zero oscillator strength). Similarly, DFT simulations show significant charge distribution of HOMO-1 and relative localization of the population in the center of molecule for HOMO. Thus, both intra-molecular optical transition and electron transfer transition between molecule and contacts will be dominated by the HOMO-1 and LUMO orbitals. Comparing HOMO-1 and LUMO (see Fig. S2) of NAB molecule, one sees that the former has a bit asymmetric spatial distribution. Thus, we set asymmetric couplings for corresponding electronic transitions:  $\Gamma_{ET_i,ET_j}^L = 0.9$  eV and  $\Gamma_{ET_i,ET_j}^R = 0.3$  eV for  $ET_{i,j} \in \{A_g \rightarrow N_x, N_g \rightarrow C_g\}$  and  $\Gamma_{ET_i,ET_j}^L = 0.6$  eV and  $\Gamma_{ET_i,ET_j}^R = 0.6$  eV for  $ET_{i,j} \in \{A_g \rightarrow N_g, N_x \rightarrow C_g\}$ . We take workfunction of the substrate to be 5.25 eV.



Figure S2: HOMO-1 (left) and LUMO (right) orbitals of neutral NAB molecule.

Regarding parameter of electron transfer between molecular units, we performed several calculations with two conjugated units and found that for dihedral angle of 129 degrees population localizes on subunits, which yields expected weakly coupled multi-unit behavior. However, pursuing *ab initio* simulations for chains is not feasible due to prohibitively large number of many-body states one needs to describe experimentally observed physics. Thus,

instead we focused on first principles simulations of the units of the chain and took an order of magnitude interaction from the corresponding Fock matrix as a parameter in our model. All parameters utilized in the simulations are collected in Table S3.

Table S3: Parameters used in the simulations

$$ET_{i,j} \in \{A_g \rightarrow N_x, N_g \rightarrow C_g\}$$

$$ET_{k,l} \in \{A_g \rightarrow N_g, N_x \rightarrow C_g\}$$

parameter	value
$\Delta_{N_g C_g}$	-3.50 eV
$\Delta_{N_x C_g}$	-0.08 eV
$\Delta_{A_g N_g}$	3.31 eV
$\Delta_{A_g N_x}$	-0.11 eV
$\Delta_{OT}$	3.42 eV
$\Gamma_{ET_i, ET_j}^L$	0.90 eV
$\Gamma_{ET_i, ET_j}^R$	0.30 eV
$\Gamma_{ET_k, ET_l}^L$	0.60 eV
$\Gamma_{ET_k, ET_l}^R$	0.60 eV
$t_{ET_n, ET_{n+1}}$	0.01 eV
$\gamma_P^{S_n}$	0.02 eV
$\gamma_{OT_n}$	14 meV
	(at $\lambda = 380$ nm)

# Hubbard NEGF method

Details of the diagrammatic technique for Hubbard NEGF can be found in ref 3. Here we give short summary of the procedure utilized for simulation of the Hubbard Green's function (eq 11 in the main text). For the problem at hand main contribution to the signal comes from single electron transfer events. Thus, for simplicity we restrict our consideration to first Hubbard approximation in which only diagrams containing bath self-energies multiplied by many-body spectral weights are taken into account as the Hubbard NEGF self-energies. Note this level of description is not capable to account for two-electron tunneling and co-tunneling; it also misses important features of noise signal. However, in calculation of fluxes dominated by single-particle transport it is sufficient.

Within the first Hubbard approximation one has to solve Dyson equation for locator

$$(i\partial_{\tau_1} - \Delta_{\mathcal{M}_1})g_{\mathcal{M}_1\mathcal{M}_2}(\tau_1, \tau_2) - \sum_{\mathcal{M}} \int_c d\tau \Sigma_{\mathcal{M}_1\mathcal{M}}(\tau_1, \tau)g_{\mathcal{M}\mathcal{M}_2}(\tau, \tau_2) = \delta_{\mathcal{M}_1, \mathcal{M}_2}\delta(\tau_1, \tau_2) \quad (\text{S1})$$

from which Hubbard Green's function is obtained by multiplication with spectral weight  $P_{\mathcal{M}_1\mathcal{M}_2}$

$$G_{\mathcal{M}_1\mathcal{M}_2}(\tau_1, \tau_2) = \sum_{\mathcal{M}} g_{\mathcal{M}_1\mathcal{M}}(\tau_1, \tau_2) P_{\mathcal{M}\mathcal{M}_2}(\tau_2) \quad (\text{S2})$$

Here

$$P_{\mathcal{M}_1\mathcal{M}_2}(\tau) \equiv \left\langle \left\{ \hat{X}_{\mathcal{M}_1}(\tau); \hat{X}_{\mathcal{M}_2}^\dagger(\tau) \right\} \right\rangle \quad (\text{S3})$$

and  $\Sigma_{\mathcal{M}_1\mathcal{M}_2}(\tau_1, \tau_2)$  is Hubbard self-energy, which consists from contributions of self-energies due to coupling to contacts ( $K = L, R$ ) and radiation field (*rad*). For chain model used in study of dependence of current o thickness of molecular layer there are also contributions from neighboring molecules in the chain ( $N$ ) and from Buttiker probes ( $P$ )

$$\Sigma_{\mathcal{M}_1\mathcal{M}_2}(\tau_1, \tau_2) = \sum_{B=L,R,rad,N,P} \Sigma_{\mathcal{M}_1\mathcal{M}_2}^B(\tau_1, \tau_2) \quad (\text{S4})$$

Following diagrammatic rules formulated in ref 3 one gets explicit expressions for the self-energies in the form

$$\Sigma_{\mathcal{M}_1, \mathcal{M}_2}^K(\tau_1, \tau_2) = \sum_{\mathcal{M}} P_{\mathcal{M}_1, \mathcal{M}} \sigma_{\mathcal{M}, \mathcal{M}_2}^K(\tau_1, \tau_2) \quad (\text{S5})$$

$$\begin{aligned} \Sigma_{\mathcal{M}_1, \mathcal{M}_2}^{rad}(\tau_1, \tau_2) &= i\pi(\tau_1, \tau_2) N_{\vec{\alpha}(\mathcal{M}_1) - \vec{\alpha}(\mathcal{O})} g_{\mathcal{M}_3^{(-)}, \mathcal{M}_4^{(-)}}(\tau_1, \tau_2) N_{\vec{\alpha}(\mathcal{M}_2) - \vec{\alpha}(\mathcal{O})} \\ &\quad + i\pi(\tau_2, \tau_1) N_{\vec{\alpha}(\mathcal{M}_1) + \vec{\alpha}(\mathcal{O})} g_{\mathcal{M}_3^{(+)}, \mathcal{M}_4^{(+)}}(\tau_1, \tau_2) N_{\vec{\alpha}(\mathcal{M}_2) + \vec{\alpha}(\mathcal{O})} \end{aligned} \quad (\text{S6})$$

$$\Sigma_{\mathcal{M}_1, \mathcal{M}_2}^N(\tau_1, \tau_2) = \sum_{\mathcal{M}} \sum_{\mathcal{M}_3, \mathcal{M}_4} P_{\mathcal{M}_1, \mathcal{M}} t_{\mathcal{M}, \mathcal{M}_3} G_{\mathcal{M}_3, \mathcal{M}_4}(\tau_1, \tau_2) t_{\mathcal{M}_4, \mathcal{M}_2} \quad (\text{S7})$$

$$\Sigma_{\mathcal{M}_1, \mathcal{M}_2}^P(\tau_1, \tau_2) = \delta_{\mathcal{M}_1, \mathcal{M}_2} \gamma_P g_{\mathcal{M}_1, \mathcal{M}_2}(\tau_1, \tau_2) \quad (\text{S8})$$

Here  $\sigma_{\mathcal{M}_1, \mathcal{M}_2}^K(\tau_1, \tau_2)$  is defined in eq 10 of the main text,

$$\pi(\tau_1, \tau_2) = \sum_{\alpha} U_{\mathcal{O}\alpha} f_{\alpha}(\tau_1, \tau_2) U_{\alpha\mathcal{O}}, \quad (\text{S9})$$

$f_{\alpha}(\tau_1, \tau_2) = -i\langle T_c \hat{a}_{\alpha}(\tau_1) \hat{a}_{\alpha}^{\dagger}(\tau_2) \rangle$  is Green's function of free photon in mode  $\alpha$ ,

$$N_{\vec{\alpha}(\mathcal{M}) - \vec{\alpha}(\mathcal{O})} \hat{X}_{\mathcal{M}^{(-)}} \equiv [\hat{X}_{\mathcal{M}}; \hat{X}_{\mathcal{O}}^{\dagger}] \quad (\text{S10})$$

$$N_{\vec{\alpha}(\mathcal{M}) + \vec{\alpha}(\mathcal{O})} \hat{X}_{\mathcal{M}^{(+)}} \equiv [\hat{X}_{\mathcal{M}}; \hat{X}_{\mathcal{O}}], \quad (\text{S11})$$

where  $N_{\vec{\alpha}}$  is equal to  $\pm 1$  when the root vector<sup>4</sup>  $\vec{\alpha}$  exists, and 0 otherwise.  $\mathcal{M}^{(+)}$  and  $\mathcal{M}^{(-)}$  are defined so as  $\vec{\alpha}(\mathcal{M}^{(+)}) = \vec{\alpha}(\mathcal{M}) - \vec{\alpha}(\mathcal{O})$  and  $\vec{\alpha}(\mathcal{M}^{(-)}) = \vec{\alpha}(\mathcal{M}) + \vec{\alpha}(\mathcal{O})$ , respectively.



## References

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