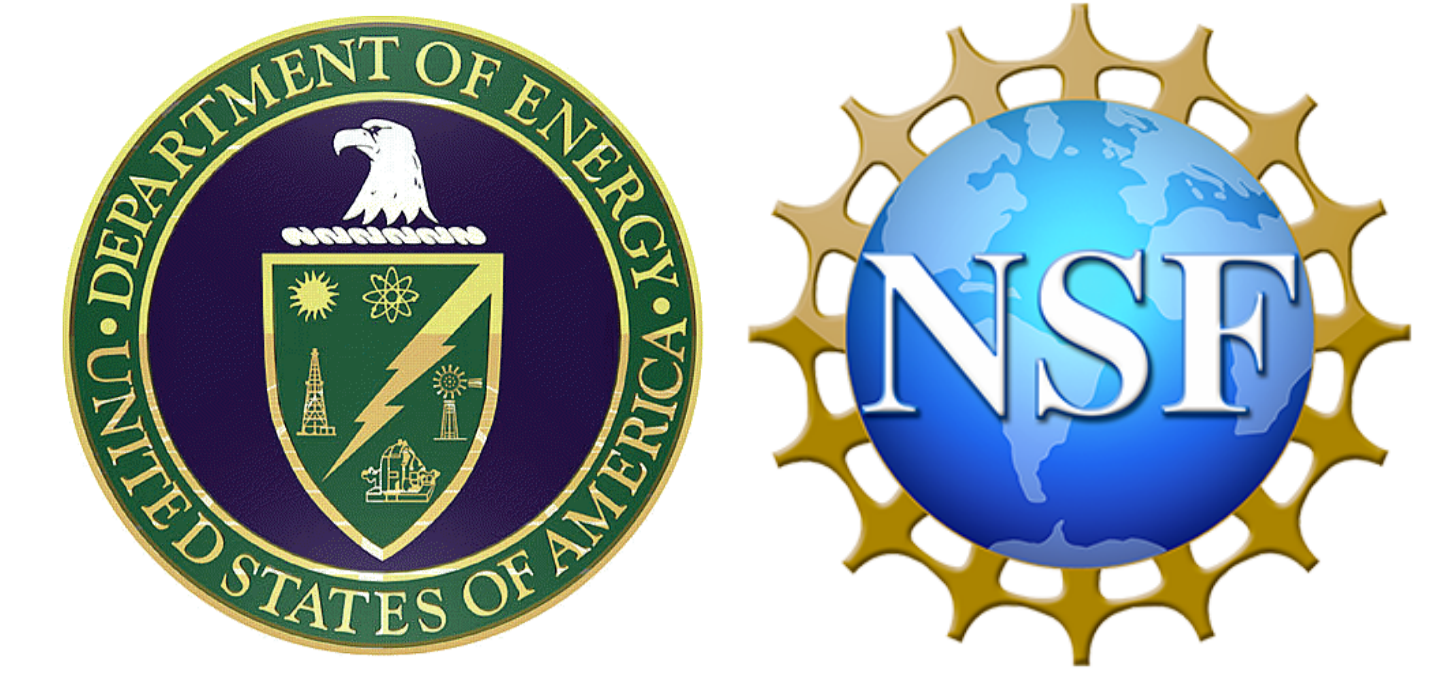# Application of the Hubbard NEGF in Molecular Optoelectronics

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Abstract

Electron transport and optical properties of a single molecule in contact with conductive materials have attracted considerable attention because of their scientific importance and potential applications. With the recent progress in experimental techniques, especially by virtue of scanning tunneling microscope (STM)-induced light emission, it has become possible to investigate single-molecule properties at subnanometer spatial resolution. Here we present a formulations of single-molecule electroluminescence driven by electron transfer between a molecule and metal electrodes and of current driven by external illumination based on a many-body state representation of the molecule. The effects of intramolecular Coulomb interaction on conductance and luminescence spectra are investigated using the nonequilibrium Hubbard Green's function technique combined with first-principles calculations. The developed theory provides a unified description of the electron transport and optical properties of a single molecule in contact with metal electrodes driven out of equilibrium, and thereby, it contributes to a microscopic understanding of optoelectronic conversion in single molecules on solid surfaces and in nanometer-scale junctions.

Hubbard NEGF Formulation

We consider a junction consisting of a molecule coupled to two electrodes and to a continuum of radiation field modes. Many-body (vibronic) states of the isolated molecule are chosen as a basis in the molecular subspace

$$|S\rangle = |e_m\rangle |v_n^{(e_m)}\rangle$$

Electron flux I_K from electrode K to the molecule and photon flux J_{ph} from the molecule into radiation field modes calculated from a generalization of the celebrated Meir-Wingreen expression

$$I_K = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} I_K(\omega) \equiv \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{e}{\hbar} \mathrm{Tr}_{\mathrm{ET}}\left[\sigma_K^<(\omega)\mathcal{G}^>(\omega) - \sigma_K^>(\omega)\mathcal{G}^<(\omega)\right],$$

$$J_{ph} = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} J_{ph}(\omega) \equiv \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{\hbar} \mathrm{Tr}_{\mathrm{OT}}\left[\sigma_{ph}^<(\omega)\mathcal{G}^>(\omega) - \sigma_{ph}^>(\omega)\mathcal{G}^<(\omega)\right].$$

Here $\sigma_K^{\lessgtr}$ and $\sigma_{ph}^{\lessgtr}$ are lesser and greater projections of the electron self-energies due to coupling to the electrode K and the radiation field. $\mathcal{G}^{\lessgtr}$ are lesser and greater projections of the molecular nonequilibrium Hubbard Green function

$$\mathcal{G}_{(S_1 S_2)(S_3 S_4)}(\tau,\tau') = -\frac{i}{\hbar}\langle T_c \hat{X}_{S_1 S_2}(\tau) \hat{X}_{S_3 S_4}^\dagger(\tau')\rangle.$$

where $\hat{X}_{S_1 S_2} = |S_1\rangle\langle S_2|$ denotes the Hubbard (projection) operator. Within the Born-Oppenheimer approximation

$$\mathcal{G}_{(S_1 S_2)(S_3 S_4)}(\tau,\tau') \approx G_{(e_1 e_2)(e_3 e_4)}(\tau,\tau')\, K_{\left(v_1^{(e_1)} v_2^{(e_2)}\right)\left(v_3^{(e_3)} v_4^{(e_4)}\right)}(\tau,\tau')$$
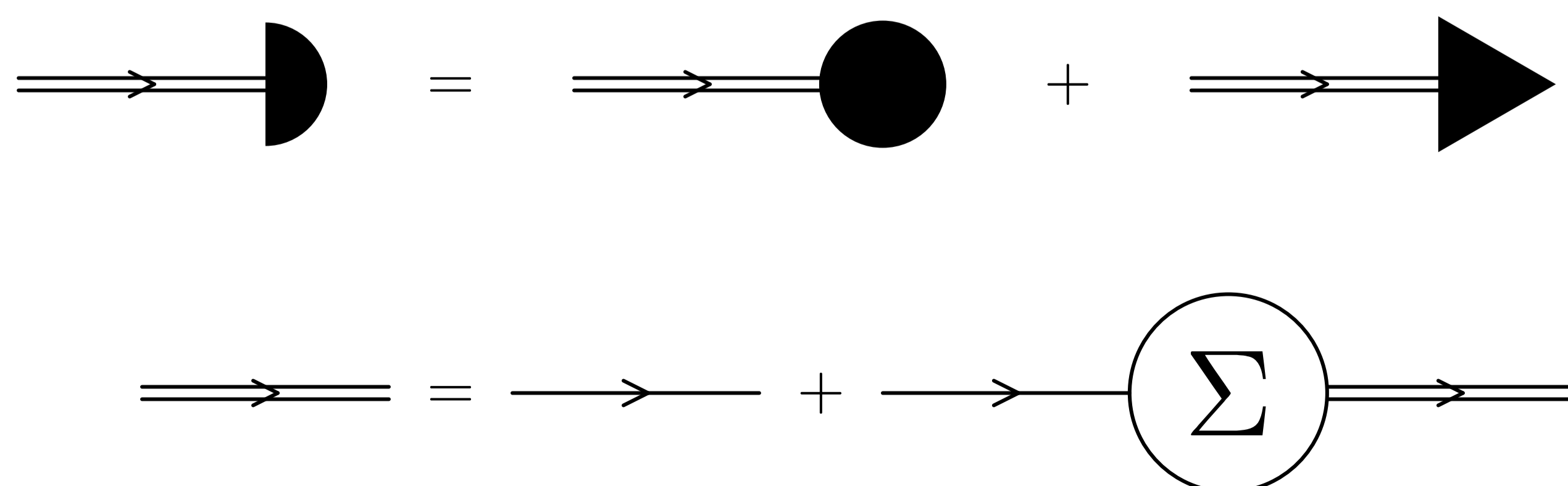
where

$$G_{(e_1 e_2)(e_3 e_4)}(\tau,\tau') = -\frac{i}{\hbar}\left\langle T_c \hat{X}_{e_1 e_2}(\tau) \hat{X}_{e_3 e_4}^\dagger(\tau')\right\rangle$$

$$K_{\left(v_1^{(e_1)} v_2^{(e_2)}\right)\left(v_3^{(e_3)} v_4^{(e_4)}\right)}(\tau,\tau') = \left\langle T_c \hat{X}_{v_1^{(e_1)} v_2^{(e_2)}}(\tau) \hat{X}_{v_3^{(e_3)} v_4^{(e_4)}}^\dagger(\tau')\right\rangle$$

Dressing K with Franck-Condon overlap integrals yields generalized Franck-Condon factor

$$FC_{\left(v_1^{(e_1)} v_2^{(e_2)}\right)\left(v_3^{(e_3)} v_4^{(e_4)}\right)}(\tau,\tau') = \langle v_1^{(e_1)}|v_2^{(e_2)}\rangle\, K_{\left(v_1^{(e_1)} v_2^{(e_2)}\right)\left(v_3^{(e_3)} v_4^{(e_4)}\right)}(\tau,\tau')\, \langle v_4^{(e_4)}|v_3^{(e_3)}\rangle$$

Green function is obtained by self-consistent solution of the modified Dyson equation.

Details of the procedure are given in Refs. [1, 2].

Bias-Induced Electroluminescence

We apply the Hubbard NEGF method to study effects of exciton binding energy on conductance and luminescence spectra. The importance of intramolecular Coulomb interaction is emphasized in explaining experimental data for a single phthalocyanine molecule, and the microscopic mechanism for electronic excitation of the molecule in STM-LE processes is proposed. Details of the study are given in Ref. [3].
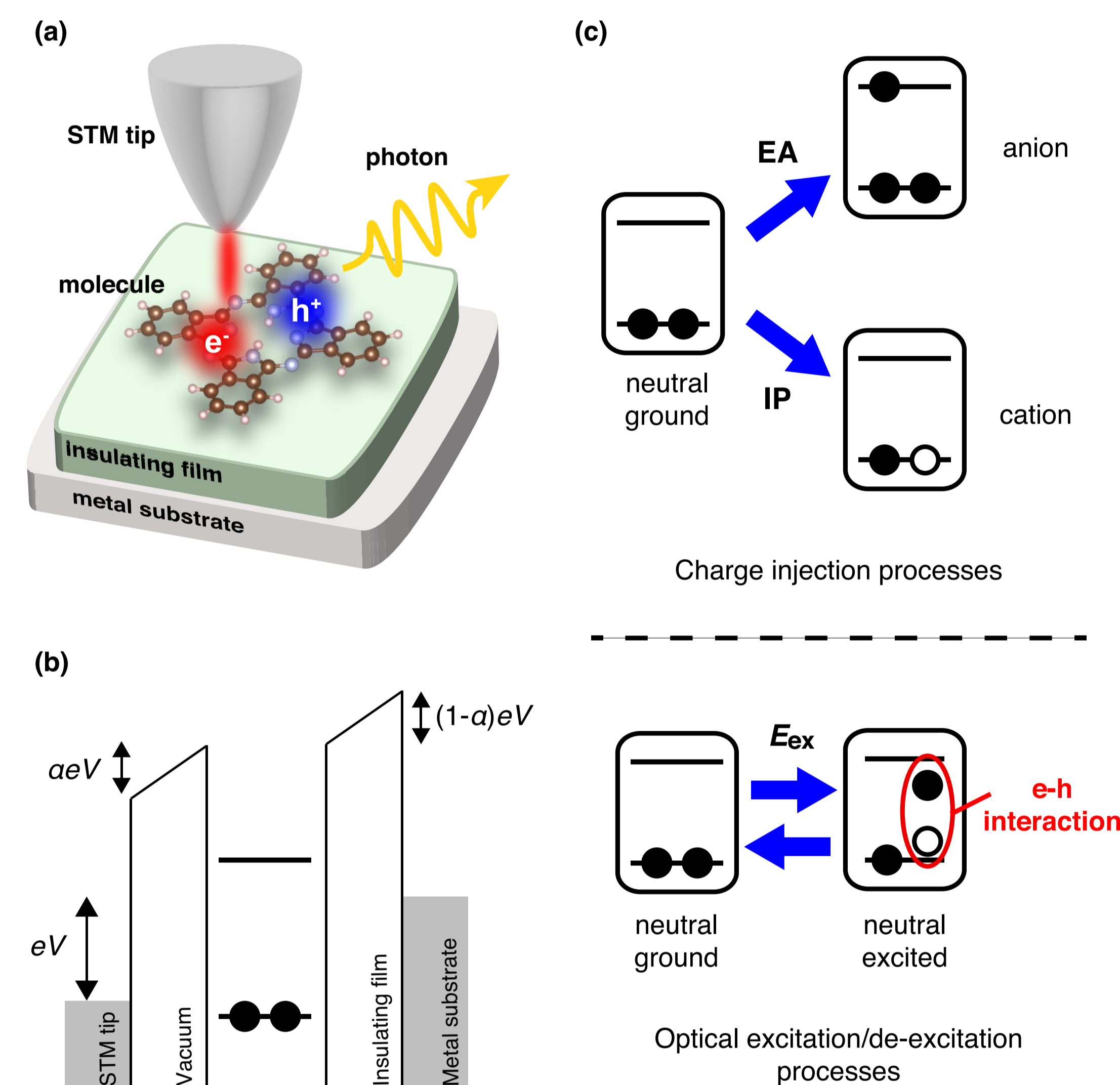

Figure 1: Schematic picture and proposed mechanism of current-driven electroluminescence for a single phthalocyanine molecule adsorbed on a few atomic layers of insulator grown on a metal substrate.
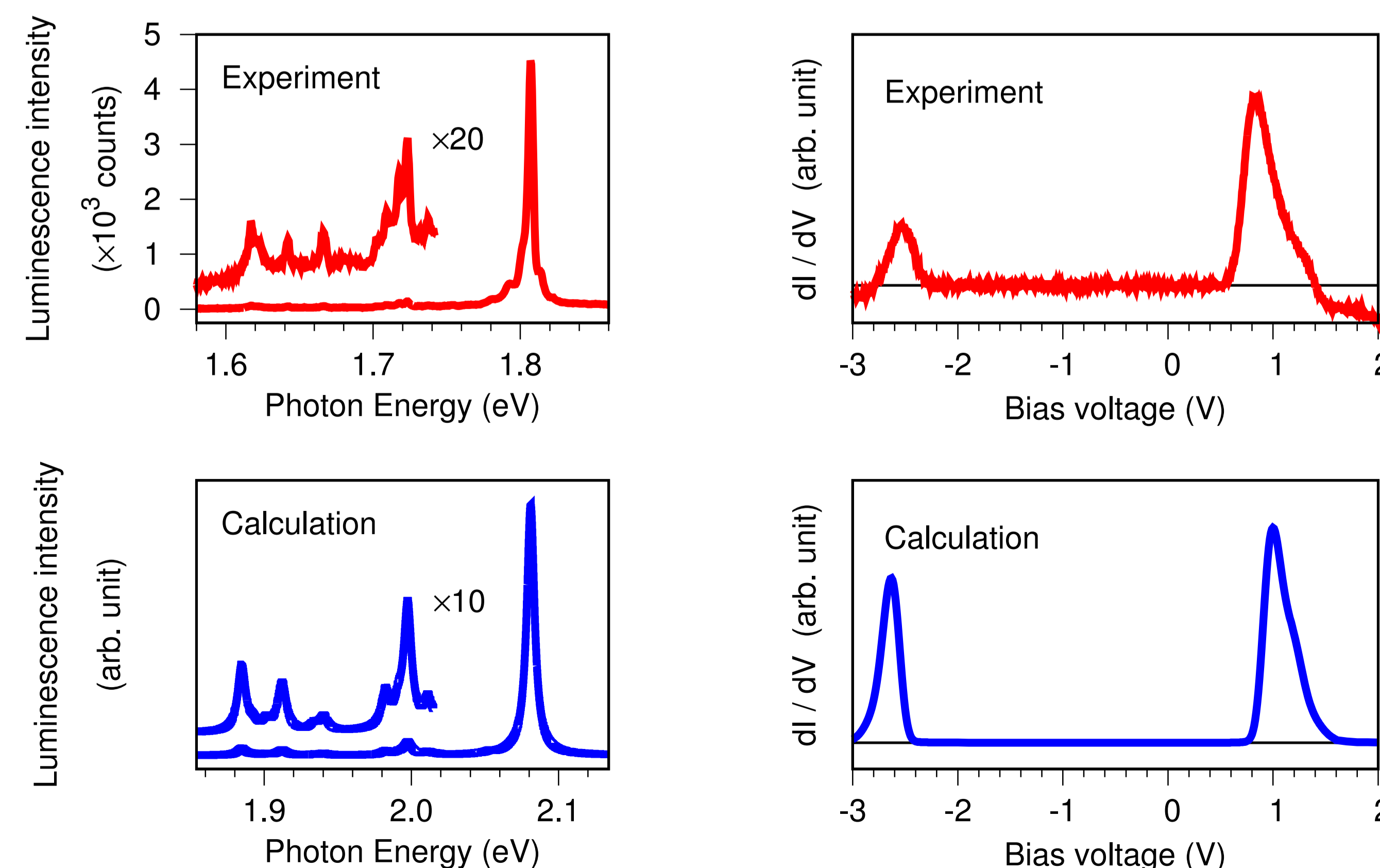

Figure 2: Luminescence spectra (left) and differential conductance dI/dV (right) obtained by STM-LE measurement (red line) and numerical calculation result (blue line).

Photo-Induced Current

We apply the Hubbard NEGF for analysis of photocurrent in nitroazobenzene molecular junction. Details of the consideration are given in Ref. [4].
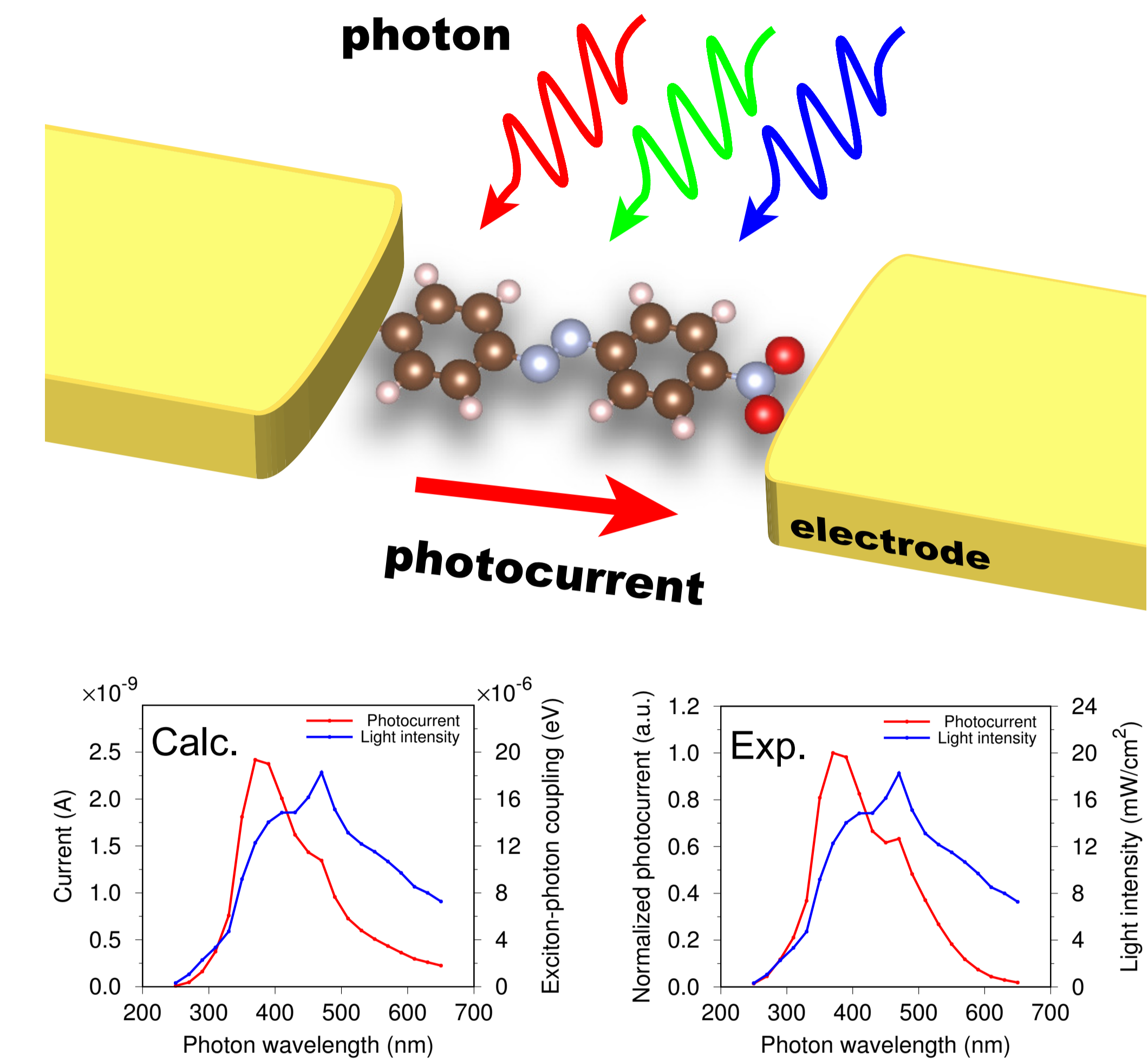

Figure 3: Schematic picture of the photo-induced current in molecular junction (top) and calculated (left bottom) and experimental (right bottom) measurements of photocurrent vs. photon wavelength.
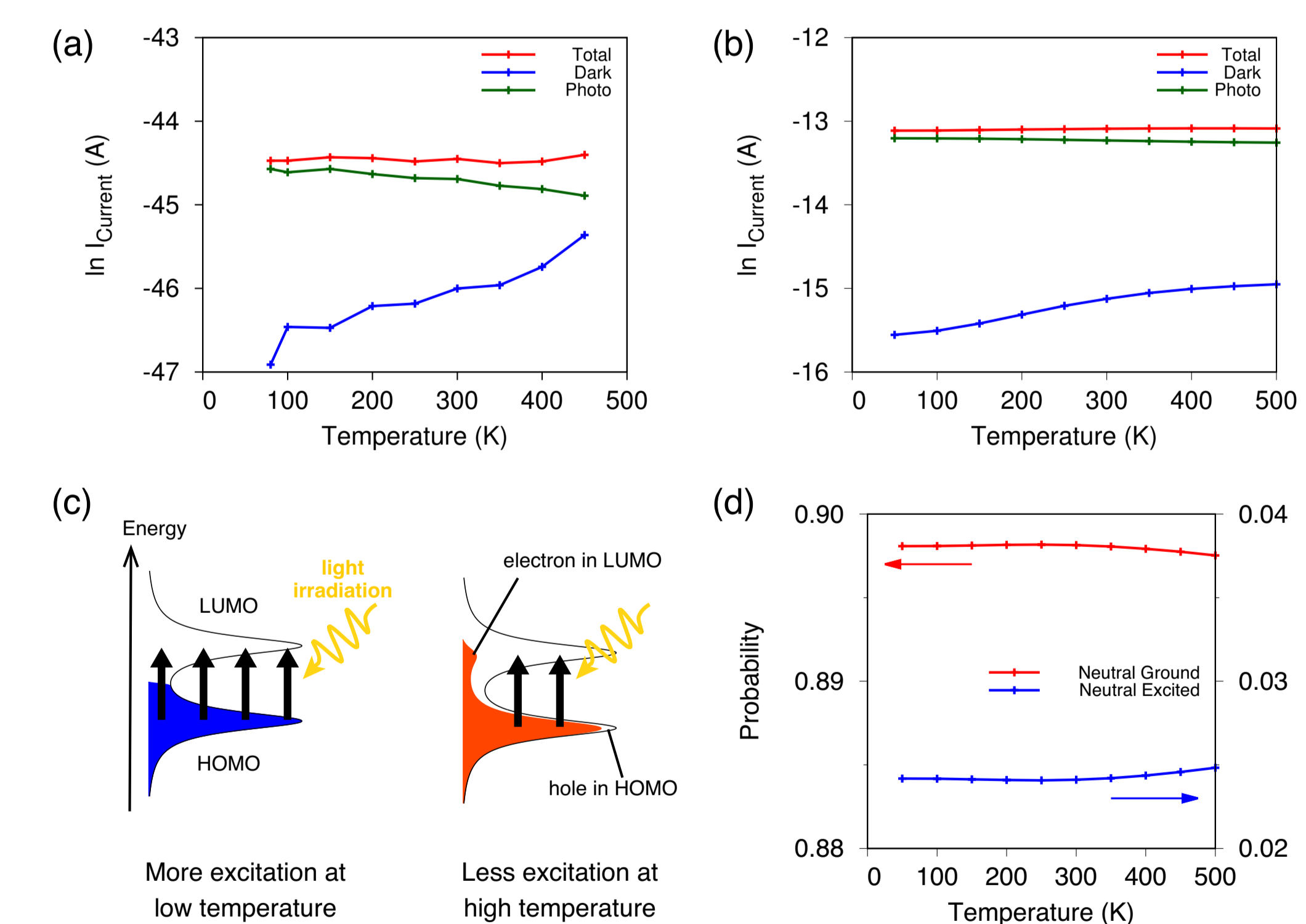

Figure 4: Temperature dependence of photo- and dark currents in biased molecular junction, $V_{sd} = 0.02$ V. Shown are (a) experimental and (b) computational results, (c) proposed mechanism, and (d) temperature dependence of populations of the neutral ground and neutral excited states.

References

[1] F. Chen, M. A. Ochoa, and M. Galperin, *J. Chem. Phys.* **146**, 092301 (2017).

[2] K. Miwa, F. Chen, and M. Galperin, *Sci. Rep.* **7**, 9735 (2017).

[3] K. Miwa, H. Imada, M. Imai-Imada, K. Kimura, M. Galperin, and Y. Kim, *Nano Lett.* **ASAP** DOI:10.1021/acs.nanolett.8b04484 (2019).

[4] K. Miwa, A. M. Najarian, R. L. McCreery, and M. Galperin, *J. Phys. Chem. Lett.* **under review** https://arxiv.org/abs/1902.02917 (2019).