The discovery of negative differential resistance (NDR) in traditional semiconductor diodes \[1\] and also organic semiconductor (OSE) nanostructures \[2, 3\] has opened a new chapter of device physics. Motivated by the potential applications of organic NDR, numerous experiments have been done with different OSE electronic devices \[4, 5, 6, 7\]. Although some possible mechanisms have been suggested, the organic NDR remains a theoretical challenge, beyond the simple picture of interband tunneling or resonant tunneling in heterostructures. The organic NDR concerns not only the excess charge transfer through lead/OSE/lead structures \[8, 9, 10\], but also the strong electron-phonon (e-ph) coupling that induces polarons in OSE structures \[11, 12\].

Historically, the discovery of magnetoresistance (GMR) effect in 1988 is considered as the beginning of a new technology called spintronics \[13, 14, 15, 16, 17\], where it is not only electron charge but electron spin that carries information. In addition to inorganic semiconductors \[18, 19\], OSE materials, due to their controllable electronic potential characteristic of a conjugated molecule, where the charge transport takes place between their \[20\] bands.

Each atomic unit in OSE is represented by a single normalized site; \( c_{n,\sigma}^\dagger \) (\( c_{n,\sigma} \)) denotes the creation (annihilation) operator of an electron at the \( n \)-th site with spin \( \sigma \), while \( \epsilon_n \), \( t_{0} \), and \( t_1 \) are the on-site energy, zero-displacement hopping integral, and nondegeneracy parameter, respectively. The lattice distortion is treated classically, in terms of the bond distances \( y_n = u_{n+1} - u_n \), deviated from its energy-minimum values that are to be determined via the Hellman-Feynman theorem [cf. Eq. (2)], with the spring constant \( K_o \) and the adiabatic e-ph coupling constant \( \alpha_o \). This is a static polaron model, which together with the effective noninteracting many-electron ansatz in Eq. (1), are considered to be justifiable in the present study of stationary transport. The effects of polaron motion and electron-electron correlation (beyond the Hartree-Fock approximation) will be the subjects of forthcoming work.

Further, we choose a symmetric ferrimagnetic (FM) \( 3d \) transition metal as electrodes. The spin-dependent charge transport takes place between their \( 3d \) bands. Neglecting spin-flip during transport and adopting the two-current model \[28\], we describe the FM metal by one-dimensional single \( d \)-band tight-binding model with a spin splitting term \[11\],

\[
H_F = \sum_{n,\sigma} \left\{ \epsilon_f d_{n,\sigma}^{\dagger} d_{n,\sigma} + t_f (d_{n,\sigma}^{\dagger} d_{n+1,\sigma} + \text{H.c.}) \right\} - \sum_n J_f (d_{n,\uparrow}^{\dagger} d_{n,\uparrow} - d_{n,\downarrow}^{\dagger} d_{n,\downarrow}),
\]

where \( d_{n,\sigma}^{\dagger} \) (\( d_{n,\sigma} \)) is the creation (annihilation) operator of an electron in the metal at the \( n \)-th site with spin \( \sigma \); \( \epsilon_f \) is the on-site energy of a metal atom, \( t_f \) is the nearest...
neighbor transfer integral, and $J_f$ is the Stoner-like exchange integral. The coupling between the OSE and FM electrodes is described by the spin-independent hopping integral, $t_{cL} = t_{cR} = \beta(t_f + t_o)$, where $\beta$ denotes the OSE-metal binding parameter.

The non-equilibrium Green’s function (NEGF) approach based on the Keldysh formalism is used to calculate the quantum transport properties of organic spintronics. To do that, the spintronic device is divided into three distinct regions. One is the so-called central scattering region (∼region), with the Hamiltonian $H_S = H_L + H_O + H_R + H_{\text{int}}$, which consists of the OSE together with a small number of metal atoms attached to each of its ends. The other two are electrodes (L and R) that serve as charge reservoirs with the steady state electronic distribution of bulk metal at given temperature. Tracing out the reservoir degrees of freedom leads to an effective ∼region Green’s function $G(E) = (E - H_S - \Sigma_L(E) - \Sigma_R(E))^{-1}$. Here, $S$ (set to be the unit matrix) is the overlap integral matrix between basis wave functions, while $\Sigma_L/R$ is the self-energy matrix that accounts for the effects of reservoir electrodes on the ∼region. It is possible to have the analytical solution of $\Sigma_L/R$ for the one-dimensional FM metal transfer-coupling with the OSE system. In this work, we adopt an efficient numerical approach through solving eigenvalue equations to achieve the self-energy. This approach can be easily extended to study the magneto-transport beyond the one-dimensional system.

The current can now be evaluated as

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} \text{Tr} \left( \Gamma_L G \Gamma_R \Gamma^\dagger \right) [f(E, \mu_L) - f(E, \mu_R)] dE. \tag{3}$$

The trace term in the integrand is the transmission coefficient function, in which $\Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger)$ denotes the broadening matrix; $f(E, \mu_L/R)$ is the Fermi distribution function at the lead chemical potential $\mu_L/R$. One can also evaluate the density of states (DOS) via

$$D(E) = i\text{Tr} \left( G(E) - G^\dagger(E) \right) / (2\pi),$$

and the reduced density matrix as

$$\rho = \frac{1}{2\pi} \sum_{\alpha=L,R,-\infty}^{\infty} G^\dagger \alpha G^\dagger f(E, \mu_\alpha) dE, \quad \tag{4}$$

with a given number of carrier electrons $N = \text{Tr} \rho$ in the ∼region. We separate the reduced density matrix into its equilibrium and bias-induced contributions, and evaluate them by contour integration and direct multi-grid Gaussian integration, respectively. Numerical implementation will be carried out in a real-function basis set representation, and the resulting $\rho$ will be real.

We take the bias $V$ not changing the electronic structures of L and R reservoirs, but just shifting their potentials by $V/2$ and $-V/2$, respectively. In contrast, it does alter the Hamiltonian of OSE to become $H_O - \phi(x)$. The electric potential drop here, satisfying $\phi(x_1) = V/2$ and $\phi(x_N) = -V/2$, should be evaluated via the potential equation with the method of images.

$$\nabla^2 \phi(x) = -\sum_{n=1}^{N_o} \frac{\rho_{n,n}}{\varepsilon_0} \delta(x_n - x), \tag{5}$$

with the charge density $\rho_{n,n}$ that depends also on $\phi(x)$, the vacuum permittivity $\varepsilon_0$, and the $n$th site coordinate $x_n = (n - 1)a$, where $a$ is the OSE lattice constant.

Furthermore, the OSE lattice distortion, which is correlated with electron wavefunctions due to the strong $c$-$ph$ interactions, is assumed to have caught up with the charge variation without dragging. The resulting lattice distortion at the finite bias voltage can therefore be evaluated via the Hellman-Feynman theorem:

$$\partial |\text{Tr}(H_S \rho)| / \partial \mu_n = 0; \text{i.e.} \ [\text{cf. Eq. (1)}],$$

$$2 \alpha_o (\rho_{n-1,n} - \rho_{n+1,n}) + K_o (y_{n-1} - y_n) = 0, \tag{6}$$

with the index $n$ including only the OSE sites, since there are no lattice distortion in the L and R sub-structures. From Eqs. (1)–(6), one can see that both the charging effect from the electrodes and the external potential from the bias voltage are all included in the non-equilibrium density matrix of the coupled $c$-$ph$ system which should be evaluated self-consistently.

There are two distinct transport measurement configurations, parallel (P) and antiparallel (AP), with respect to the relative magnetization orientation of two FM electrodes. Generally, in the two-current model, both the majority-majority and minority-minority (or majority-minority and minority-majority) transports are permitted in the P (or AP) configuration. But for the cobalt electrodes in the present work, the full-filled up-spin electrons cannot transport under in the P-configuration and the charge carriers are only the half-filled down-spin electrons. Contrary, the charge carriers in the AP-configuration under $V > 0$ are only the up-spin electrons, driven from the full-filled majority-spin band of L-electrode to the half-filled minority-spin band of R-electrode of opposite magnetization orientation.

We are now in the position to elucidate numerically the $I$-$V$ characteristics, especially the NDR behavior of OSE systems. The SSH parameters for the OSE system [Eq. (1)] are $\epsilon_o = -4.3$ eV, $t_o = 2.5$ eV, $t_1 = 0.04$ eV, $\alpha_o = 5.0$ eV/$\text{Å}$, and $K_o = 0.11$ eV/$\text{Å}^2$, which are the modified values from those of conducting polymers, for the OSE being of larger band gap. The tight-binding parameters for the cobalt electrodes [Eq. (2)] are $\epsilon_f = -7.0$ eV, $t_f = 1.5$ eV and $J_f = 1.45$ eV, determined by fitting the cobalt 3$d$ band structure. The OSE-metal binding parameter $\beta$ will be specified later.

To justify the above values, we calculated the band structures of the model OSE and FM cobalt electrodes individually (with $\beta = 0$); see Fig. 11, for their resulting DOS at $T = 11$ K. Our model OSE of 10 sites has the highest occupied and lowest unoccupied molecular orbitals of $E_{\text{HOMO}} = E_F - 0.9$ eV and $E_{\text{LUMO}} = E_F + 2.0$ eV.
eV, where $E_F$ is the Fermi level of the cobalt electrode. These results well reproduce the band gap diagram of the OSE spin-valve device used in a recent experiment \(22\). The model cobalt metal is also consistent with the real material \(23\), which shows one full-filled majority-spin band, and one half-filled minority-spin band.

Let us start with the equilibrium property of the model spintronic system at $V = 0$, at which the S-region (Co/OSE/Co) assumes charge neutral. In our model, the S-region consists of a cobalt oligomer of 10 sites to each terminal of the 10-site OSE; thus each segment in Co/OSE/Co involves 20 spin-orbitals. If the OSE-metal binding parameter $\beta = 0$, three segments of the S-region would be charge neutral individually, with $N_k = N_R = 15$ and $N_O = 10$ electrons, respectively. In reality $\beta \neq 0$ and intra-regional charge transfer (ICT) is possible. Depicted in Fig.1, is the calculated DOS of the organic spintronic device with the OSE-metal binding parameter $\beta = 0.5$, where an ICT of about 1.14e from OSE to Co-segments has occurred. The observed ‘self-doping’ phenomenon here is largely due to the strong e-ph interaction, which leads to the formation of a preexisting hole polaron that stabilizes the S-region complex before applying potential bias \(24\). The preexisting polaron state is rather evident by examining the majority-spin band of Co/OSE/Co complex (solid-curve in Fig.1b), since its isolated metal counterpart (thick-solid curve in Fig.1b) is completely filled up to the Fermi level.

We then calculated the $I-V$ characteristic [Eq.3] of the model Co/OSE/Co spintronics at $T = 11$ K and $\beta = 0.5$, in both the P and AP configurations of relative magnetization orientation of FM electrodes. The resulting $I-V$ curves in these two configurations (P: solid; AP: dash) are shown in Fig.2a, and the corresponding $dI/dV$ ones are in Fig.2b. Included in Fig.2b is also a thick-curve for the bias voltage dependence of magnetoresistance (MR), $\Delta R/R = (R_{AP} - R_P)/R_{AP}$, measuring the relative difference of electric resistance with these two configurations.

Consider first the NDR behavior (about $-26.3$ kΩ at its minimum) in the P-configuration, where the current, after an initial near-ohmic increase, drops quickly from $I_{peak} = 4.45$ μA at $V_{peak} = 0.35$ V to $I_{valley} = 0.49$ μA at $V_{valley} = 0.4$ V. To see what happens during the NDR region, we also examined other nonequilibrium properties (at $V > 0$). Shown in Fig.3 are the representing results of both the current peak (solid) and valley (dash) states: (a) the majority-spin (up-spin) DOS $D(E)$; (b) the P-configuration (down-spin) transmission coefficient function $T(E)$. Indicated in Fig.3 are also the numbers of electrons in the OSE segment at the two corresponding voltages. By checking the charge distribution and the lattice distortion (not shown here), we found: (i) The preexisting hole polaron remains localized around the OSE center when $0 \leq V \leq V_{peak}$; (ii) As $V$ increases further, the excess electron charge migrates from the leads into the OSE segment; and (iii) At $V_{valley} = 0.4$ V, the preexisting hole is completely annihilated, and the OSE is essentially in its dimerized ground charge-neutral state.

The above observations suggest that the NDR behavior in the P-configuration, shown by the solid curves in Fig.2a, is due to the annihilation of the preexisting, ‘self-doping’ polaron. As discussed earlier (cf. Fig.1b), the preexisting hole polaron level at $V = 0$ deeply localizes in the down-spin band (P-configuration conduction band) gap of the OSE, which leads to its relatively large DOS, and thus a low-resistance state according to the doping theory of conducting polymers \(34\). This accounts for the rapid increase of current when $V < V_{peak}$ in the P-configuration (the solid curve in Fig.2a). Figure3 shows clearly that the increase of bias voltage from $V_{peak}$ to $V_{valley}$ accompanies with the annihilation of the preexisting polaron, which accounts for the NDR observed in the P-configuration (solid curves) in Fig.2a.

In the AP configuration, the charge carriers at $V > 0$ are no longer the down-spin electrons, but the up-spin ones, from the majority subband of L to the minority subband of R electrode. As the observed switch-on voltage in this case (about 0.5 V) exceeds the aforementioned NDR region, the ‘preexisting polaron’ makes no direct contribution to the conductance in the AP configuration. The resulting $I-V$ characteristic (dash-curve in Fig.2b) can thus be all understood (including its switch-on voltage) by examining the structures of the two involving subbands in Fig.1a at $V = 0$.

Finally, let us make comments on the voltage-dependent MR (the thick-curve in Fig.2b), especially the negative GMR of $(\Delta R/R)_{max} = 300\%$ at $V = 1.1$ V. Negative MR has been experimentally observed in the Co/SrTiO$_3$/LSMO tunnel junction \(37\) and the LSMO/OSE/Co spin-valve device \(22\). Traditionally, one analyses the observed MR, or other transport behavior as function of bias potential, via the involving DOS of conduction bands/subbands of uncorrelated ($\beta = 0$) FM/OSE/FM systems at $V = 0$, such as Fig.1a and Ref.33. This traditional analysis does lead to our understanding the qualitative MR-V behavior in each individual voltage range in Fig.2b, where $\Delta R/R$ decreases from 100% changes sign into the negative MR region, reaches $(\Delta R/R)_{max}$ at $V = 1.1$ V, and etc. However, the quantitative GMR values in Fig.2b, especially its maximum value of 300%, cannot be accounted for via the simple band structure analysis with $\beta = 0$ and/or $V = 0$. The calculated extraordinary GMR of 300% can only be accounted for via the ‘self-doping’ of preexisting polaron and its annihilation that affect distinctly differently on conductances depending on the (P or AP) relative magnetization orientation of FM electrodes.

In summary, we proposed to exploit ‘self-doping’ FM$_1$/OSE/FM$_2$ structures for distinct NDR and GMR materials. Numerical demonstrations were performed based on a realistic model system. The theoretical NDR was found as a result of transition from the low-resistant preexisting hole (cation) polaron to high-resistant dimerized charge-neutral ground state. This NDR mechanism is different from the two-step reduction picture, proposed...
originaly by Reed and Tour and co-workers\textsuperscript{2} in explaining their experiment on a redox-center-containing molecule, in which NDR results as transition from conducting anion to insulating dianion state. As it appears in the P- but not AP-configuration of relative magnetization orientation of FM electrodes, the NDR leads also to a large magnitude (300\%) of negative GMR, much larger than the experimentally reported ones by far\textsuperscript{22}. Many OSEs are easy-doping materials\textsuperscript{34}, and the required ‘preexisting polaron’ state can be formed in either self-doping or external doping manner. Thus, experimental realizations of GMR far exceeding 100\% in organic spintronic devices should be feasible according to the present model study.

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\begin{thebibliography}{99}
\bibitem{1} S. M. Sze, \textit{High-Speed Semiconductor Devices} (Wiley Press, New York, 1990).
\bibitem{2} J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science \textbf{286}, 1550 (1999).
\bibitem{3} J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, D. W. Price, and J. M. Tour, Appl. Phys. Lett. \textbf{77}, 1224 (2000).
\bibitem{4} I. Kratochvilova, M. Kocirik, A. Zambova, J. Mbindyo, T. E. Mallouk, and T. S. Mayer, J. Mater. Chem. \textbf{12}, 2927 (2002).
\bibitem{5} K. Walzer, E. Marx, N. C. Greenham, R. J. Less, P. R. Raithby, and K. Stokbro, J. Am. Chem. Soc. \textbf{126}, 1229 (2004).
\bibitem{6} A. M. Rawlett, T. J. Hopson, I. Amlani, R. Zhang, J. Treschk, L. A. Nagahara, R. K. Tsui, and H. Goronkin, Nanotechnology \textbf{14}, 377 (2003).
\bibitem{7} A. M. Rawlett, T. J. Hopson, I. Amlani, R. Zhang, J. Treschk, L. A. Nagahara, R. K. Tsui, and H. Goronkin, Nano Lett. \textbf{4}, 55 (2005).
\bibitem{8} Y. Xue, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. B \textbf{59}, R7852 (1999).
\bibitem{9} Y. Karzazi, J. Cornil, and J. L. Brédas, Nanotechnology \textbf{14}, 165 (2003).
\bibitem{10} E. G. Emberly and G. Kirchenow, Phy. Rev. B \textbf{64}, 125318 (2001).
\bibitem{11} S. J. Xie, K. H. Ahn, D. L. Smith, A. R. Bishop, and A. Saxena, Phy. Rev. B \textbf{67}, 125202 (2003).
\bibitem{12} M. Galperin, M. A. Ratner, and A. Nitzan, Nano Lett. \textbf{5}, 125 (2005).
\bibitem{13} M. N. Baibich, J. M. Broto, A. Fert, F. N. V. Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. \textbf{61}, 2472 (1988).
\bibitem{14} J. Barnas, A. Fuss, R. E. Camley, P. Grünberg, and W. Zinn, Phys. Rev. B \textbf{42}, 8110 (1990).
\bibitem{15} J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. \textbf{74}, 3273 (1995).
\bibitem{16} S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Mottnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science \textbf{294}, 1488 (2001).
\bibitem{17} I. Žutić, J. Fabian, and S. D. Sarma, Rev. Mod. Phys. \textbf{76}, 323 (2004).
\bibitem{18} J. M. Kikkawa and D. D. Awschalom, Nature \textbf{397}, 139 (1999).
\bibitem{19} S. S. Yan, C. Ren, X. Wang, Y. Xin, Z. X. Zhou, L. M. Mei, M. J. Ren, Y. X. Chen, Y. H. Liu, and H. Garmestani, Appl. Phys. Lett. \textbf{84}, 2376 (2004).
\bibitem{20} V. I. Krinichnyi, Synth. Met. \textbf{108}, 173 (2000).
\bibitem{21} V. Dediu, M. Murgia, F. C. Matarotta, C. Taliani, and S. Barbanera, Solid State Commun. \textbf{122}, 1811C184 (2002).
\bibitem{22} Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, Nature \textbf{427}, 821 (2004).
\bibitem{23} W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B \textbf{22}, 2099 (1980).
\bibitem{24} H. J. Torii, J. Phys. Chem. A \textbf{104}, 413 (2000).
\bibitem{25} J. H. Wei, S. J. Xie, S. G. Wang, and M. L. Mei, Phys. Lett. A \textbf{292}, 207 (2001).
\bibitem{26} E. M. Conwell and S. V. Rakhmanova, Proc. Natl. Acad. Sci. USA \textbf{97}, 4556 (2000).
\bibitem{27} J. H. Wei, L. X. Wang, K. S. Chan, and Y. Yan, Phys. Rev. B \textbf{72}, 064304 (2005).
\bibitem{28} A. Fert, J. Phys. C \textbf{2}, 1784 (1969).
\bibitem{29} L. V. Keldysh, Sov. Phys. JETP \textbf{20}, 1018 (1965).
\bibitem{30} S. Datta, \textit{Electronic Transport in Mesoscopic Systems} (Oxford University Press, New York, 1995).
\bibitem{31} M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B \textbf{65}, 165401 (2002).
\bibitem{32} T. Ando, Phys. Rev. B \textbf{44}, 8017 (1991).
\bibitem{33} J. D. Jackson, \textit{Classical electrodynamics} (Wiley, New York, 1975).
\bibitem{34} A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. \textbf{60}, 781 (1988).
\bibitem{35} D. A. Papaconstantopoulos, \textit{Handbook of the Band Structure of Elemental Solids} (Plenum Press, New York, 1986).
\bibitem{36} J. L. Brédas and G. B. Street, Acc. Chem. Res. \textbf{18}, 309 (1985).
\bibitem{37} J. M. De Teresa, A. Barthélémy, A. Fert, J. P. Contour, R. Lyonnet, F. Montaigne, P. Seneor, and A. Vaurès, Phys. Rev. Lett. \textbf{82}, 4288 (1999).
\end{thebibliography}
FIG. 1: DOS of the majority-spin (solid-curves) and minority-spin (dash-curves) bands of model systems: (a) The isolated OSE (thick-curves) and Co 3d band (thin-curves), with the OSE-metal binding parameter $\beta = 0$; (b) The binded Co/OSE/Co spintronic device with $\beta = 0.5$. Temperature $T = 11$ K.

FIG. 2: (a) The $I$-$V$ characteristics of the Co/OSE/Co system in Fig 1b, measured with the P- (solid-curve) and AP-configuration (dash-curve) of relative magnetic orientation of electrodes. (b) The $dI/dV$, obtained numerically via (a), and $-\Delta R/R$ (thick-line) as functions of the bias voltage.
FIG. 3: The current-peak state (solid-lines) and the valley state (dash-lines), referring to the $I$-$V$ characteristc of the parallel configuration in Fig. 2a, in terms of (a) the DOS of majority-spin band, and (b) the transmission coefficient of electrons (minority-spin). The total numbers of electrons in the OSE segment in the current-peak and valley states are specified.