# Calculating the Number of Conduction Channels in a Single-Electron Reservoir Network Based on a Metal-Organic Framework Polymer

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**Abstract**—The density functional theory is used to obtain single-particle spectra of fragments of the onedimensional metal—organic chain of a coordinated polymer. The effective resistance of the organic part of the polymer is calculated, along with the characteristic Coulomb energy and the effective capacitance of the charge center. The number of conduction channels in an experimentally studied reservoir network based on the observed polymer chains is estimated.

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### **INTRODUCTION**

The technological capabilities of manufacturing basic functional elements in large-scale and highly efficient modern integrated microcircuits have almost reached the atomic scale, but the simplest and most miniature functional elements in such microcircuits are still tens of nanometers in size. Increasing the circuit density of such elements will require moving to devices in which the basic functional elements consist of single or small groups of atoms and are actually nanoscale electronic devices with atomic functional structures. Atomic and molecular single-electron structures (nanoscale electronic devices that operate on the basis of new physical principles) are therefore of particular interest [1]. In such devices, charges are transferred by single electron tunneling. A key feature of such devices is strong Coulomb effects that include a correlation between charge tunnel transfer and the Coulomb blocking of tunnel currents at some distributions of additional and polarization charges on working atoms and molecules [2, 3].

Single-electron reservoir computer networks, which are compact and have new functional properties, are devices that use a specially created distribution of molecules on the surface of a dielectric, or impurity atoms in the surface layer of a semiconductor. The structures described in [4, 5] were examples of such devices. Those works presented single-electron devices based on disordered systems of charge centers consisting of gold nanoclusters and boron impurity atoms in a silicon substrate, respectively. The singleelectron reservoir networks in [4, 5] were systems of charge centers localized within regions 100–200 nm in diameter, interconnected by means of tunnels and surrounded by a system of control nanoelectrodes. The number of charge centers in the working areas of such devices can range from tens to tens of thousands, depending on the distance between electrodes and the types of centers that are used.

The mechanism of single-electron reservoir network operation is setting the potential relief in the region of charge center localization using control electrodes and controlling the charges induced at the centers. Such control allows us to activate different groups of charge centers and charge states by opening some tunneling channels and closing others. The values of the potentials needed for one function or another of the reservoir network are determined by machine learning [4]. Single-electron transport in such structures is therefore controlled and they are programmed to perform various logic functions.

On the one hand, a supercompact single-electron reservoir network is a universal multicontact, dynamically reconfigurable analog element that can be used to create similar binary and ternary logic elements [4], nonlinear analog functional elements, and charge and electric field sensors. On the other hand, such singleelectron reservoir networks can be used as neural networks [6] for recognizing images or modeling the activity of the brain there when it is too complicated or expensive to use conventional electronics or program analogs [5]. However, the active internal structure of the charge centers in such devices is strongly disordered, which negatively affects the predictability and repeatability of a system's internal transport processes and functional properties.

Metal-organic frameworks (MOFs) can be used to create single-electron reservoir networks with ordered structures of charge centers [7]. These are porous crystalline materials in which metal ions or other polynuclear inorganic clusters are interconnected by means of organic molecules called ligands. Coordination bonds form between organic and inorganic components through electrons being donated and accepted by atoms [8]. The use of metal-organic framework polymers allows us to create supercompact nanoelectron reservoir networks with one-, two-, and threedimensional ordered arrangements of charge centers that are needed to obtain stable characteristics in future devices with atomic functional structures. MOF polymers also have properties that can be of use to researchers in the field of nanoelectronics [9]. MOFs can be synthesized on working surfaces by means of self-assembly, which could simplify the technology of manufacturing devices based on them. The wide variety of ligands and metal centers allows us to select polymers with desired properties, structure, and dimension suited to a concrete problem [7]. MOFs are also modifiable and can reversibly change their properties under external impacts.

MOF polymers are already widely used as active structures in numerous devices. For example, a monatomic single-electron transistor based on one link of an MOF with metal centers on cobalt and rhodium ions separated from control electrodes by ligands was described in [10, 11]. Using a gate, the authors were able to control the single-electron current in the system up to room temperature and vary the device's characteristics by choosing the ligands and metal centers. MOFs can also be used to construct two- and three-dimensional systems of molecular cubits [12, 13]. There are many proven ways of depositing MOFs that allow us to synthesize a given system on almost any substrate [14]. Due to the ordered and reconfigurable structure of MOFs, we can control the number of cubits and the distances between them. Some polymers have long periods of spin-lattice relaxation even at room temperature [14], setting a high limit for a cubit's period of coherence that determines the stability of its state and the number of errors when operating with it. Due to the porosity of the material, the molecules of analyzed substances can penetrate into the polymer, allowing us to detect biochemical agents with the help of cubits [15]. MOFs are also successfully employed in indirect scintillation [16] and radiation detectors [17]. It is important that MOFs can also be used as active elements of sensor devices. The polymers can respond to such external impacts as changes in temperature, pressure, electromagnetic fields, or the chemical environment [9]. The authors of [18] described an electron sensor based on protein nanowires modified by attractor molecules assembled in large arrays. The structure of the sensor allowed the nanowire to be replaced with a one-dimensional MOF chain that could improve the device's characteristics [9]. Due to their variability, metal–organic network polymers have nearly unlimited potential for modification that can expand the scope of substances detectable by one sensor [7].

Preliminary estimates show that using an MOF as an active component of a single-electron reservoir network would allow the working temperature to reach the level of room temperature. The mechanism of the device's operation would not change appreciably, since the metal centers of the MOF would form a network of isolated monatomic charge centers between which charge carriers will tunnel. However, the small size and low capacitances of the charge centers would produce great changes in the charge energies of electron tunneling:

$$\Delta E = \frac{e^2}{2C},\tag{1}$$

where *C* is the effective self-capacitance of a charge center [19] and *e* is the electron charge. This would ensure small thermal fluctuations with energy  $k_{\rm B}T$ , where  $k_{\rm B}$  is the Boltzmann constant and *T* is temperature; the observability of one-electron effects; and stable operation of the device even at room temperature.

We performed a theoretical study of the conductive properties of a metal—organic one-dimensional network polymer closing a system of control nanoelectrodes in a single-electron reservoir network. We considered a one-dimensional MOF in which the organic ligand connecting two separated charge centers (atoms of copper (II)) was terpyridine (see Fig. 1b). The onedimensional MOF was chosen as the initial object of research since it is a simpler chemical compound for preparing and calculating its model properties.

# CALCULATION PROCEDURE

We performed a theoretical study of the MOFbased single-electron reservoir network presented schematically in Fig. 1a [20]. One-dimensional MOFs represented by the green lines and red dots were deposited onto a system of gold nanoelectrodes arranged in a circle with a minimum distance of 40 nm between them. The red dots represent charge centers consisting of copper atoms surrounded by ligand shells (terpyridine). The number of charge centers in Fig. 1a does not correspond to a real system, since the number of charge centers (copper atoms) in even the shortest MOFs connecting neighboring electrodes is at least 15. The structural formula of one link of an MOF with two charge centers is shown in Fig. 1c. Such links connected in sequence form the structure of a one-



**Fig. 1.** (a) Scheme of the investigated single-electron reservoir network based on an MOF (top view). Triangles represent nanoelectrodes arranged on a nonconducting solid-state substrate; the green lines are the MOF and the red dots are charge centers on copper ions with terpyridine ligands. (b) Schematic image of a polymer chain and its components. (c) Structural formula of an MOF link. (d) 3D image of an MOF link.

dimensional MOF (i.e., one conductive channel). Since one-dimensional MOFs are deposited arbitrarily onto the nanoelectrodes in a real experiment, some deposited molecules may not close the nanoelectrodes if they are fixed to them by only one end. The resistance measured at each pair of electrodes is inversely proportional to the number of MOF channels closing them. It is determined by the resistance of each MOF channel, which is in turn determined by the number of links in each MOF channel and the penetrability of the tunnel potential barrier in each link [21]:

$$\frac{1}{R_{ij}} = \sum_{\alpha}^{N_{ij}} \frac{1}{R_{ij,\alpha}} = \sum_{\alpha}^{N_{ij}} \frac{1}{n_{ij,\alpha}r} = \tau G_0 \sum_{\alpha}^{N_{ij}} \frac{1}{n_{ij,\alpha}},$$
(2)

where  $R_{ij}$  is the resistance measured between electrodes *i* and *j*;  $N_{ij}$  is the number of MOFs closing electrodes *i* and *j*;  $R_{ij,\alpha}$  is the resistance of one MOF channel;  $n_{ij,\alpha}$  is the number of links in the channel with index  $\alpha$  connecting electrodes *i* and *j*;  $\tau$  is the penetrability of the tunnel barrier between two neighboring charge centers of the MOF; and  $G_0 = e^2/h$  is the quantum of conductivity. Expression (2) shows that the main contribution to the conduction between the pair of electrodes *i* and *j* is made by the channels that close them and have the lowest number  $n_{ij,\alpha}$ . Assuming that the MOF channels have roughly identical minimum lengths, expression (2) can be approximated as

$$\frac{1}{R_{ij}} \approx \tau G_0 \frac{N_{ij}}{\langle n_{ij,\alpha} \rangle},\tag{3}$$

where  $\langle n_{ij,\alpha} \rangle$  is the average number of links in the MOF. Expression (3) can be used to estimate the number of channels closing each pair of electrodes if penetrability  $\tau$  of the tunnel barrier between neighboring charge centers is known. An exact value of the coefficient of penetrability of the tunnel barrier between neighboring charge centers can be calculated using a transfer matrix [22]. We can use the formula for a rectangular potential barrier with the equivalent area to obtain an approximation:

$$\tau \approx 1 / \left( 1 + \frac{U_0^2 \sin h^2(\kappa a)}{4E(U_0 E)} \right),$$

$$\sqrt{2mU_0}a = \int_{x_1}^{x_2} \sqrt{2m(U(x) - E)} dx,$$
(4)

where  $U_0$  and *a* are the height and width of the equivalent rectangular tunnel barrier; *E* and *m* are the energy and mass of a tunneling electron;  $\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$  is the constant of sub-barrier attenuation; and U(x) is the distribution of the effective potential between neighboring charge centers. This distribution is calculated from data on the distribution of electron density and the positions and charges of nuclei, which can be calculated with quantum-chemical packets.

In this work, we used an approach based on formula (3) to calculate the resistance of one MOF channel. At the first stage, we considered a fragment of an MOF consisting of two charge centers of copper. Each charge center was a coordination bond of a copper ion



Fig. 2. Components of the investigated MOF: a charge center on a copper ion with terpyridine ligands (on the left) and an effective tunnel barrier formed by a butane-containing fragment of an MOF with the indicated chemical elements and characteristic sizes.

surrounded by two ligands of terpyridine with benzene molecules (Fig. 2). The structure of the molecules is shown in Figs. 1c and 1d. It is formed by two charge centers bound to butane through oxygen atoms. Information taken from the Cambridge Crystallographic Data Center's was used to determine the atomic structure of this fragment of the MOF. This fragment of the MOF was subdivided into two components in order to determine its resistance: the charge center, which consisted of conductive benzene rings, terpyridine, and a copper atom, and the nonconductive butane-containing fragment with joint atoms of oxygen that operates as a tunnel barrier. In this work, we determined the effective potential barrier geometrically from the nonconductive fragment (butane and atoms of oxygen) between charge centers. Delocalization on this fragment was not possible, since it had only single covalent chemical bonds and the corresponding single-particle electron spectrum.

We used the NWChem program complex [23] and the density functional theory (DFT) to calculate the single-particle electron energy spectra for each such fragment of an MOF link. The magnitude of total energy E(n) for charge states n = -3...+3, where n > 0 means no electrons and n < 0 is an excess of electrons in the fragment. In our calculations for MOFs, we used the B3LYP functional and the 6-31G atomic basis for all atoms of fragments. According to Koopman's theorem [24], the *i*th ionization potential of a fragment, which is also the chemical potential in the corresponding charge state, can be determined as

$$I_{n} = \mu_{n} = E(n) - E(n-1).$$
 (5)

The values of  $I_n$  for a negative *n* determine the affinity toward electrons:

$$A_{-n+1} = I_n, \text{ for } n \le 0.$$
 (6)

According to Koopman's theorem, if we use a continuum to represent the reference level of energy, the position of the *i*th single-particle level in the spectrum can be written as

$$\varepsilon_i = -I_i. \tag{7}$$

If a fragment of a molecule is in a state with the minimum multiplicity, single-particle electron energy level  $\varepsilon_1$  is simultaneously the upper filled single-particle electronic state  $\varepsilon_1 = \varepsilon_{HOMO}$ . Level of energy  $\varepsilon_0 = \varepsilon_{LUMO}$  corresponds to the lower unfilled energy state. Value *n* of the effective capacity in charge state is determined as [19]

$$C_n = \frac{e^2}{\mu_{n+1} - \mu_n} = \frac{e^2}{E_{n+1} + E_{n-1} - 2E_n}.$$
 (8)

# **RESULTS AND DISCUSSION**

Calculated values of the total energy of fragments of an MOF link with a charge center are presented in Fig. 3a. We can see that dependence E(n) has a characteristic inflection at point n = 0, due to the two upper filled single-particle valent energy levels of the fragments with charge centers being linked to the localized states on a copper ion. The unfilled levels correspond to the ligand shell. The calculated singleparticle electron energy spectra of a molecular fragment of a charge center and tunnel barrier are shown in Fig. 3b. The position of the upper filled energy level of the fragment with the charge center relative to the continuum is  $\varepsilon_{HOMO} = -4.2$  eV. The shape of the electron single-particle spectrum of the fragment with a charge center relative to the single-particle electron spectrum of a nonconducting fragment allows us to estimate the height of the effective potential barrier for electron tunneling from one copper ion to another. We can see from the presented spectrum that the noncon-



**Fig. 3.** Dependences of the total energy of a fragment of an MOF with a copper charge center on charge state *n*. (a) Blue segments show differences in the total energy corresponding to the ionization potentials and illustrating calculations of the single-particle spectrum. (b) Hartree–Fock-like single-particle electron energy spectrum of MOF fragments, obtained with the DFT. Filled and unfilled levels are marked in red and green, respectively.

ducting fragment has no neighboring single-particle states near level  $\varepsilon_{HOMO}$ . The lowest filled level of this fragment is  $\varepsilon_{HOMO}^{TB} = -8$  eV, and the highest unfilled level is  $\varepsilon_{LUMO}^{TB} = +3$  eV. The most probable mechanism of charge transfer is therefore electron tunneling through a barrier with height  $U_0 \sim 4.2$  eV, determined by a nonconducting ligand with no localization ("attendance") at transient single-particle states.

We can estimate the penetrability of an MOF link using expression (4) and known values of tunnel barrier height  $U_0 \approx 4.2$  eV and width  $a \approx 3.9$  nm, which is approximately equal to the length of a nonconducting fragment of the MOF. The estimate obtained for the penetrability of the effective tunnel barrier is  $\tau = 6 \times 10^{-3}$ . The effective resistance of one MOF link calculated with formula (3) is  $R_0 \approx 4.3$  MOhm, evidence that the resistance between two charge centers corresponds with a good margin to the condition of small quantum fluctuations of the charge for singleelectron tunneling [25].

To calculate the self-capacitance of the charge center on a copper ion, we use expression (1) and the obtained Hartree–Fock-like energy spectrum of the charge center (Fig. 3b). The value of the HOMO– LUMO gap of an MOF fragment with charge center  $E_C = \varepsilon_{LUMO} - \varepsilon_{HOMO} \approx 4.9$  eV allows us to estimate the effective capacitance of the charge center and the radius of localization of the additional electron:  $C \approx 3.8 \times 10^{-20}$  F and  $r_C = C/4\pi\epsilon_0 = e^2/4\pi\epsilon_0 E_C \approx$ 3.4 Å, respectively. This estimate of radius  $r_C$  of localization applies to a conductive sphere with a capacitance equal to the effective capacitance of the charge center. For purposes of comparison, Fig. 2 shows a circle with a radius of 3.4 Å, superimposed onto an MOF fragment with a metal charge center.

The expression obtained for the Coulomb energy exceeds by more than two orders of magnitude the average energy of thermal fluctuations at room temperature:

$$E_C \approx 4.9 \text{ eV} \gg k_{\rm B}T \approx 26 \text{ meV},$$
 (9)

thereby satisfying the condition of small thermal fluctuations and ensuring the existence of Coulomb effects in such systems at this temperature [25].

Based on our results, we also estimated the value of the tunnel matrix element used in the expression for the Fermi golden rule [22] for the rates of tunneling:

$$\Gamma = \frac{2\pi}{\hbar} |T|^2 \,\delta(E_{\rm f} - E_{\rm i} - \Delta F), \qquad (10)$$

where  $\Gamma$  is the rate of tunneling;  $E_i$  and  $E_f$  are the energy of the initial and final states of a tunneling electron; and  $\Delta F$  is the change in the free energy of the system during tunneling. We can determine  $\Gamma$  in this expression by estimating the frequency of electron motion in a region with a characteristic size whose order of magnitude is the same as the radius of localization of additional electron  $r_C$  on the charge center and the tunnel barrier penetrability:

$$\Gamma \sim \nu \tau. \tag{11}$$

We can estimate the frequency of revolution of a nonrelativistic electron from the energy of dimensional quantization in a potential well with size  $2r_c$ :

$$v = \frac{\hbar}{4mr_c^2} \approx 2.5 \times 10^{14} \text{ s}^{-1}.$$
 (12)

Our estimate for the rate of tunneling at such a frequency of revolution is

$$\Gamma \sim \nu \tau \approx 1.5 \times 10^{12} \text{ s}^{-1}.$$
 (13)

Finally, the value of the tunnel matrix element can be determined as

$$\left|\tilde{T}\right| \sim \hbar\Gamma \approx 1 \text{ meV.}$$
 (14)

These estimates allow us to determine the extent to which the valence levels in the metal charge center broaden due to quantum fluctuations of the charge. Note that  $|\tilde{T}| \ll k_{\rm B}T$  at room temperature, so the main contribution to the broadening of the charge center's valent energy levels is made by thermal fluctuations.

#### CONCLUSIONS

Resistance  $R_0 = 4.3$  Mohm obtained for one MOF link allows us to determine the resistance of an entire MOF chain. For a chain with the minimum length connecting neighboring nanoelectrodes *i* and *j* and consisting of 15 links, this resistance is  $R_{ij} = 64.5$  MOhm. An MOF chain that can close distant electrodes of the reservoir network and contain 80 and more links has resistance  $R_{ij} \ge 344$  MOhm. Based on the theoretical size of one MOF link and the interelectrode resistance measured in our experiment with a single-electron reservoir network, we calculated the possible number of conduction channels (the number of conducting chains). The considered system (see Fig. 1) was found to contain four conduction channels 45 nm long and ten that were 100 nm long.

The observability of the single-electron effects in a system based on coordination links in which terpyridine, benzene, oxygen, and butane are organic ligands and copper ions are metal centers was confirmed experimentally at room temperature [20]. The calculations performed in this work theoretically confirm this possibility.

Single-particle spectra of fragments of a compound based on terpyridine with two specific monatomic charge centers were obtained using the density functional theory. The conduction properties of this compound were investigated, and the penetrability of the effective tunnel barrier determined by a nonconducting butane-containing segment was calculated. The resistance of one link of the MOF was determined and used to estimate the resistances of MOF chains of different lengths. We obtained the effective capacitance and radius of localization of an additional electron on a charge center based on a copper atom. The theoretical possibility of observing single-electron effects in a system based on the considered compound at room temperature was predicted. The numbers of conducting chains of different lengths were estimated for a multielectrode nanoelectron system closed by a group of one-dimensional MOF chains consisting of the investigated linking compounds.

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