

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263938982>

Surprising Molecular Length Dependence in Conduction through a Hybrid Organic–Inorganic System

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JUNE 2013

Impact Factor: 7.46 · DOI: 10.1021/jz400943q

CITATION

1

READS

22

3 AUTHORS, INCLUDING:



Sivan Kober

biofeed

2 PUBLICATIONS 22 CITATIONS

SEE PROFILE



Ron Naaman

Weizmann Institute of Science

304 PUBLICATIONS 5,388 CITATIONS

SEE PROFILE

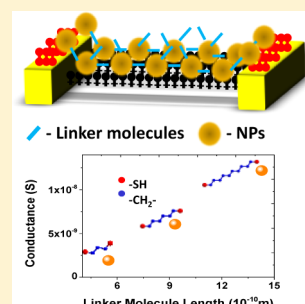
Surprising Molecular Length Dependence in Conduction through a Hybrid Organic–Inorganic System

Sivan Kober, Gilad Gotesman, and Ron Naaman*

Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

S Supporting Information

ABSTRACT: A hybrid device made from gold nanoparticles connected by alkyldithiol molecules of different lengths was produced and its conduction properties were investigated for various lengths of the organic linker molecules. It was found that the conductivity increases with the length of the molecules. The surprising dependence of the conductivity on the molecules' length was explained by a model that takes into account the probability for forming continuous conductive paths for the different molecules.



SECTION: Physical Processes in Nanomaterials and Nanostructures

Conduction properties of organic molecules have been the focus of many studies for years. The interest in this subject results from two origins: the first is the need for a basic understanding of the electronic properties of organic molecules, and the other stems from the idea that one may introduce interesting optoelectronic properties to electronic devices by using organic molecules. However, in practice, the subject was found to be quite complex due to the need to make a well-defined and reproducible contact between the organic and the inorganic, typically metal, electrodes and due to the molecular conformation, which is not always controllable.

It is well-established that because those molecules are in general poor conductors, the conductivity decreases exponentially for short-range conduction and may decrease as a power law for longer ranges. This is indeed what has been observed by studying either conduction through single molecules or through self-assembled monolayers (SAMs).

One approach suggests that hybrid devices may be used for introducing the properties of organic molecules to electronic devices, where organic molecules are mixed with metal nanoparticles (NPs).^{1–3} There are two NP-based techniques: in the first, a dimer of NPs is connected by a bifunctional molecule (or an ensemble of molecules). Although in this method the NP–molecule structure is reproducible,⁴ the contact between the NPs and the electrode is less controlled and is not well-defined. The second technique consists of two electrodes separated by a small gap, covered by a SAM, whereas metal NPs are deposited to bridge the gap.^{2,5–7} Extension of the second method includes microscale devices that employ metal NPs mixed with organic molecules.^{8–12} Here the main goal is to better understand the conduction mechanisms in the whole assembly and to probe how it is affected by the molecular properties. Indeed, in this case, one does not obtain

the details observed when studying single-molecule-based devices.

In the present work, we investigated the effect of the length of saturated organic molecules on the conduction properties of hybrid devices. The device is based on mixing gold NPs (GNPs) with alkanedithiols of different lengths, 1,3-propanedithiol, 1,6-hexanedithiol, and 1,10-decanedithiol (C₃DT, C₆DT, and C₁₀DT, respectively, Figure 1a), and depositing the hybrid mixture between two electrodes positioned 2 μm apart. The current versus voltage curves (*I*–*V*) were measured for different lengths of alkanedithiols. As a reference, devices with alkanemonthiols (C_{*x*}MT) of lengths similar to the alkanedithiols were also measured. Because a large ensemble of molecules and GNPs is measured, the effect of the molecular structure is expressed by averaging the conduction properties of the entire ensemble.

It will be shown that in such hybrid devices the molecule-length dependence of the conduction is not trivial and it deviates dramatically from the expectations based on the single-molecule properties.

A microelectronic interdigitated device was built containing 33 pairs of electrodes (dimensions: 200 μm in length and 150 nm in height) with a total overlap length of 6600 μm and a 2 μm gap (Figure 1b). The devices were prepared by a conventional photolithography procedure on glass substrates and coated with a hybrid film containing alkanedithiols and GNPs. The NPs were synthesized following the recipe described in the Supporting Information, and their size was verified by their plasmon resonance peak (Figure 2a).

Received: May 5, 2013

Accepted: June 4, 2013

Published: June 4, 2013

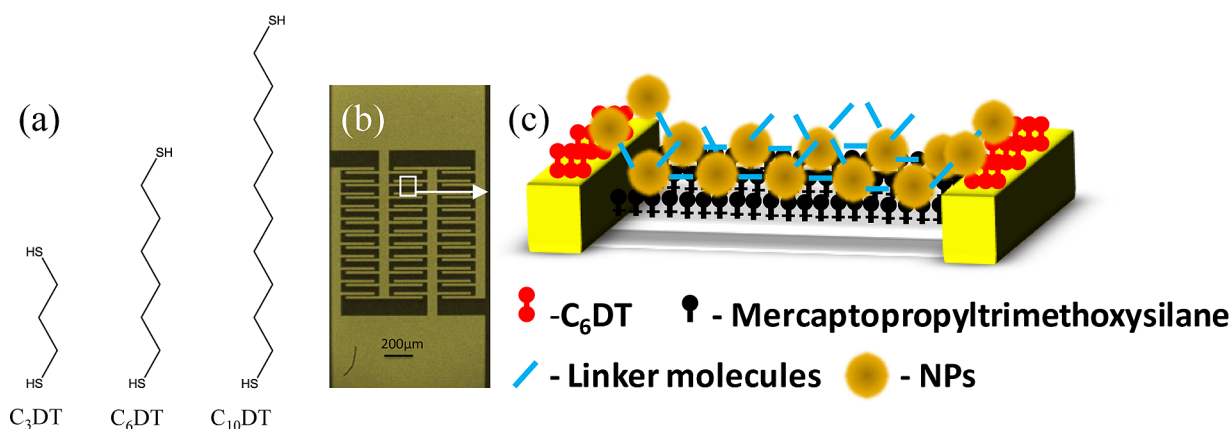


Figure 1. (a) Alkanedithiol molecules used in this work: 1,3-propanedithiol (C₃DT), 1,6-hexanedithiol (C₆DT), and 1,10-decanedithiol (C₁₀DT). (b) Device image, taken by light microscope. The yellowish area is the gold electrodes. (c) Scheme of the single device coated with the hybrid organic-GNPs film.

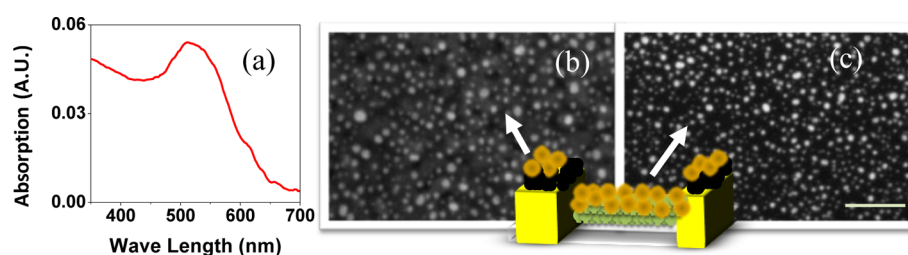


Figure 2. (a) GNP surface plasmon resonance absorption. The peak location indicates that the GNP size can be up to 40 nm. (b,c) SEM images of GNP layers on a gold substrate (the electrodes) covered with a C₆DT monolayer (b) and on silicon substrate (the gap between the electrodes) covered with a MPS monolayer (c). Scale bar is 100 nm. The scheme between panels b and c shows the location of the probed layers on the device.

The production procedure of the device (Figure 1c) was based on functionalizing the device's surface by an organic molecule SAM.¹³ In brief, a SAM of 1,6-hexanedithiol was adsorbed on the gold electrode, and a SAM of 3-mercaptopropyltrimethoxysilane (MPS) was adsorbed on the SiO₂ gap between the electrodes. Then GNPs were self-assembled on the functionalized device. Finally, alkanedithiols were adsorbed on the GNPs.

The adsorption of the GNPs was characterized by scanning electron microscopy (SEM). Samples of GNPs adsorbed on C₆DT SAM on gold and on MPS SAM on silicon were prepared by the same procedure used for producing the devices. Figure 2b,c shows characteristic SEM images of these samples. These images indicate that the particle diameter ranges from 5 to 15 nm. Another important observation is that the GNPs do not create a highly packed layer on either substrate. However, the method for device production is important technologically because it is very simple (alternating dipping of the device in various solutions) and robust.

When the device is measured as is, with no GNP and molecules, its conduction is extremely low. The results of the electrical measurements performed on the hybrid devices are presented in Figure 3. The characteristic *I*–*V* curve was found to be symmetric; therefore, only the current obtained for the positive potential (between 0 and 3 V) is shown. The stability under voltage bias was tested for each device.

Figure 3a shows the results from three measurements taken consecutively on the same device, consisting of a GNP monolayer and a C₃DT linker layer. Figure 3b presents the *I*–*V* curves for three different devices, either containing only the GNP monolayer (red curves) or with a GNP monolayer

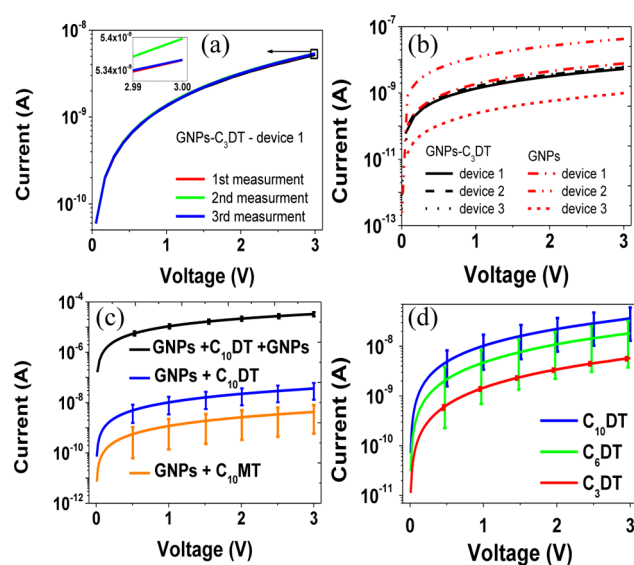


Figure 3. (a) Current versus voltage (*I*–*V*) measurements performed three times on the same device, which consists of a GNP layer and C₃DT linker layer on top. (The inset shows that indeed the three curves fall almost exactly one on top of each other). (b) *I*–*V* curves obtained for three devices of a GNP monolayer and three devices of a GNP monolayer and a C₃DT linker layer. (c) *I*–*V* curves of a device in which the GNPs are linked by C₁₀MT (orange), C₁₀DT (red), and a C₁₀DT linked bilayer (black). (d) *I*–*V* curves of devices consisting of a monolayer of GNPs linked by different molecules: C₃DT, C₆DT, and C₁₀DT.

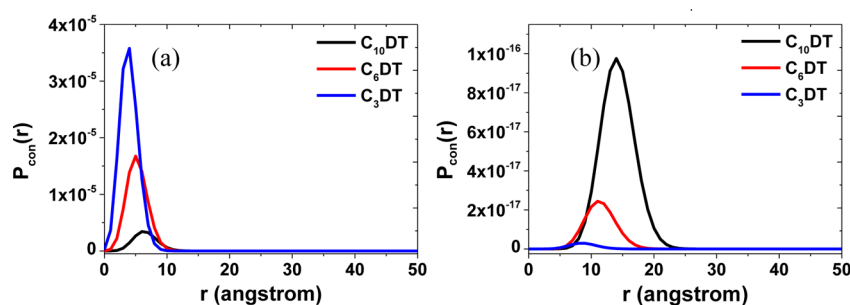


Figure 4. Calculated conduction probability (P_{con}) through the hybrid device containing the alkanedithiol molecules, as a function of the distance, for an average particle distance $\lambda_p = 11$ (a) and 50 Å (b).

and a C_3 DT linker layer (black curves). These measurements indicate that the devices are stable with consecutive measurements and that the devices made with the linker layer have reproducible conductivity. In comparison, the devices made of a GNP monolayer alone show great diversity in their conductivity. To determine the role and importance of the chemical binding of the alkanedithiol linkers to the GNPs, we measured the conductivity of devices made of a GNP monolayer with alkanemonthiol and with an alkanedithiol linker layer and in addition devices in which we added a second GNP layer on top of the alkanedithiol linker layer. Figure 3C shows the I versus V curves for a device with a GNP monolayer with decanemonthiol (C_{10} MT) and a C_{10} DT linker layer and devices with a bilayer of GNPs linked with C_{10} DT. It is clear that the chemical binding between the GNPs in the monolayer, when using DT linkers, contributes to the conduction through the layer and that the addition of a second layer of NPs significantly increases the conductivity. Figure 3d shows the average of the I – V curves for devices coated with a GNP monolayer linked with alkanedithiol of different lengths. The average was performed on three devices from each type (for each linker). Surprisingly, the conduction increases with the increasing length of the alkanedithiol chain length.

The above results prove that by using our procedures a large number of hybrid electronic devices can be produced with robust properties. They show reproducible conductivity and great stability under ambient conditions and under applied voltage. When the device is made from a single monolayer of GNPs, it is conductive, but the conductivity varies significantly between devices. When a linker of alkanethiol molecules is added to the GNP monolayer, the conductivity becomes highly uniform and is consistent among many devices. When the linker is alkanedithiol, the conductivity is higher than in the case of alkanemonthiol of the same length. This is most probably because of the dithiolated molecules linking adjacent NPs in the film. Namely, the connectivity between the GNPs by the alkanedithiols significantly improves the conductivity of the device. Our main and most surprising finding is that the conductivity increases with the length of the alkanedithiol molecules.

These observations can be rationalized by a model that takes into account the fact that the NPs are not closely packed on the surface and that the distances are distributed between them. This nonuniform organization of the NPs is indeed observed in SEM images. The other assumption, included in the model, assumes that conduction through the linker organic molecule can be described by tunneling. Hence, conduction through the hybrid device is based on tunneling between the NPs through the organic linker and hopping between the NPs.

The uneven distribution of the NPs on the device's surface causes the irreproducible conductivity in the case of devices made of a single monolayer of GNPs. This is due to variations in the number of conducting paths available for the electrons moving in the layer. As we add the linker molecules, there are more conduction paths because the organic molecules may link more than one GNP to each GNP. As a result, the number of available conducting paths increases.

Considering only the tunneling part of the model, one would expect that electron transport through long molecules will be less efficient than through short ones. Here we observed the opposite trend, which can be rationalized by the fact that in the hybrid system the conduction is controlled by the available conducting paths.

In this model we assume that the probability of an electron to traverse the film from one electrode to the other (P_{con}) depends on three parameters: the GNPs' distribution in the layer (the distance between the particles), the distribution of the molecules' length, and the probability of tunneling through the organic molecules. The distribution of the molecule's length arises from the different configurations each alkyl chain can adapt, which result in some variation in length even though all molecules in a given device have the same number of carbons. Furthermore, we assume an equal amount of bonded linker molecules, independent of the linker length. Thiol binding to the GNP is a very reactive and fast process, and it is expected that all of the free sites on the surface of the NPs were occupied by the alkylthiols, independent of their length.

Hence, P_{con} can be expressed as a product of three functions: two Poisson distributions: one describing the distances between the GNPs (P_p) and the other relating to the molecular length (P_m). The third function is the probability of an electron tunneling through the organic molecule (P_t):

$$P_{\text{con}}(r) = P_p(r, \lambda_p) \cdot P_m(r, \lambda_m) \cdot P_t(r, \beta)$$

$$P_{\text{con}}(r) \propto \frac{\lambda_p^r}{r!} e^{-\lambda_p} \cdot \frac{\lambda_m^r}{r!} e^{-\lambda_m} \cdot e^{-\beta r} \quad (1)$$

where r is the length of the organic molecule, λ_p is the average distance between the GNP, and λ_m is the average length of the molecule. β is the tunneling decay parameter, which equals $\sim 1 \text{ Å}^{-1}$ for alkyl chains.^{14,15} λ_m is taken as 0.8 of the full molecule length due to the molecules not being necessarily stretched. The theoretical lengths of the linkers were calculated by Chemdraw to be 14.28, 9.32, and 5.5 Å for C_{10} DT, C_6 DT, and C_3 DT, respectively. The integral over P_{con} is proportional to the current for the given parameters.

Figure 4 shows the P_{con} distribution curves for two average distances between the particles 11 (Figure 4a) and 50 Å (Figure

4 b), representing highly and moderately packed GNP layers, respectively.

The most prominent difference between the two plots is the peak height for the different molecules. In the highly packed layer, all three molecules have a high probability of binding two neighboring GNPs. Therefore, the conduction probability is dictated mainly by tunneling, which decreases exponentially with the molecule length, making the shortest molecule, C₃DT, the one with the highest conduction probability.

For moderately packed layers, the longer molecule has a higher probability of binding two neighboring GNPs and thus of creating a full conduction path through the film. As a result, the peak corresponding to C₁₀DT is the highest. In addition, the P_{con} values decrease dramatically as the distance between the GNPs increase due to both the reduced tunneling probability and an absolute decrease in the binding probability for all molecules.

Figure 5 offers a closer look at the influence of the layer density (λ_p) on conduction by presenting the dependence of

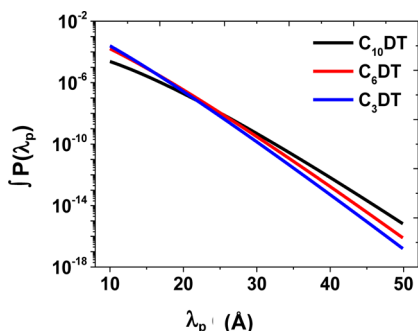


Figure 5. Calculated integral over the conduction probability for the alkanedithiol molecules, as a function of the average particle distance.

the integral over P_{con} as a function of the average distance between the GNP for the three alkanedithiol molecules. There are three distinct regions: $\lambda_p < 16$ Å, $16 < \lambda_p < 25$ Å, and $\lambda_p > 25$ Å. As shown in Figure 4, the first region is characterized by the highest conduction probability for C₃DT (Figure 4a), whereas in the third zone the highest conduction probability is for C₁₀DT (Figure 4b). In the intermediate region, there is no clear dependence of the conduction on the molecular length. In general, as the layer of GNP becomes less packed, P_{con} decreases for all molecules.

The mechanism proposed here that takes into account the probability of formation of continuous conduction path is of course related to the organization of the NPs. For a highly ordered system, it is expected that when the molecular length exceeds the average distance between the NPs a sharp increase in the conductivity will be observed. However, the current results are expected for systems characterized by large variation in the distances between the NPs.

The results presented are consistent with the recent description of the cotunneling transport mechanisms in hybrid organic–inorganic devices.^{16,17} This mechanism is similar to the hopping mechanism in electron transfer through molecules, but it is based on Coulomb blockade in the small metal NPs and tunneling between those NPs.

In summary, we characterized the electronic properties of a hybrid device made from GNPs connected by alkyldithiol molecules having different lengths. The surprising dependence of the conductivity on the molecules' length was explained by a

simple model that takes into account the probability of forming a continuous conductive path for the different molecules. The model demonstrates a trend that fits our results when the average particle distance between the GNPs is larger than 23 Å. As shown by the SEM images of the film, this parameter properly describes the distance distribution among the GNPs in the devices. The model also predicts a trend opposite of what we have found for dense GNP layers with average particle distances smaller than 16 Å. This prediction fits a previous experiment, where it was found that in a layer of GNPs linked by alkanedithiol the shorter the alkanedithiol is, the higher the conduction is.¹²

■ ASSOCIATED CONTENT

Supporting Information

Production of the device and the control experiments performed.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Eran Bouchbinder for helpful advice regarding the model. This work was partially supported by the Israel Science Foundation and by the U.S. Department of Energy (grant no. ER46430).

■ REFERENCES

- (1) Dadosh, T.; Gordin, Y.; Krahne, R.; Khivrich, I.; Mahalu, D.; Frydman, V.; Sperling, J.; Yacoby, A.; Bar-Joseph, I. Measurement of the Conductance of Single Conjugated Molecules. *Nature* **2005**, *436*, 677–680.
- (2) Amlani, I.; Rawlett, A. M.; Nagahara, L. A.; Tsui, R. K. An Approach to Transport Measurements of Electronic Molecules. *Appl. Phys. Lett.* **2002**, *80*, 2761–2763.
- (3) Brust, M.; Bethell, D.; Kiely, C. J.; Schiffrin, D. J. Self-Assembled Gold Nanoparticle Thin Films with Nonmetallic Optical and Electronic Properties. *Langmuir* **1998**, *14*, 5425–5429.
- (4) Na, J.-S.; Ayres, J.; Chandra, K. L.; Chu, C.; Gorman, C. B.; Parsons, G. N. Conduction Mechanisms and Stability of Single Molecule Nanoparticle/Molecule/Nanoparticle Junctions. *Nanotechnology* **2007**, *18*, 035203.
- (5) Long, D. P.; Patterson, C. H.; Moore, M. H.; Seferos, D. S.; Bazan, G. C.; Kushmerick, J. G. Magnetic Directed Assembly of Molecular Junctions. *Appl. Phys. Lett.* **2005**, *86*, 153105.
- (6) Chu, C.; Na, J.-S.; Parsons, G. N. Conductivity in Alkylamine/Gold and Alkanethiol/Gold Molecular Junctions Measured in Molecule/Nanoparticle/Molecule Bridges and Conducting Probe Structures. *J. Am. Chem. Soc.* **2007**, *129*, 2287–2296.
- (7) Bolotin, K. I.; Kuemmeth, F.; Pasupathy, A. N.; Ralph, D. C. Metal-Nanoparticle Single-Electron Transistors Fabricated Using Electromigration. *arXiv:cond-mat/0310594* **2003**, DOI: 10.1063/1.1695203.
- (8) Liao, J.; Bernard, L.; Langer, M.; Schönenberger, C.; Calame, M. Reversible Formation of Molecular Junctions in 2D Nanoparticle Arrays. *Adv. Mater.* **2006**, *18*, 2444–2447.
- (9) Taniguchi, S.-I.; Minamoto, M.; Matsushita, M. M.; Sugawara, T.; Kawada, Y.; Bethell, D. Electron Transport in Networks of Gold Nanoparticles Connected by Oligothiophene Molecular Wires. *J. Mater. Chem.* **2006**, *16*, 3459–3465.
- (10) Chen, S. Langmuir Monolayers of Gold Nanoparticles: From Ohmic to Rectifying Charge Transfer. *Anal. Chim. Acta* **2003**, *496*, 29–37.

- (11) Leong, W. L.; Lee, P. S.; Mhaisalkar, S. G.; Chen, T. P.; Dodabalapur, A. Charging Phenomena in Pentacene-Gold Nanoparticle Memory Device. *Appl. Phys. Lett.* **2007**, *90*, 042906.
- (12) Snow, A. W.; Ancona, M. G.; Kruppa, W.; Jernigan, G. G.; Foos, E. E.; Park, D. Self-Assembly of Gold Nanoclusters on Micro- and Nanoelectronic Substrates. *J. Mater. Chem.* **2002**, *12*, 1222–1230.
- (13) Gotesman, G.; Guliamov, R.; Naaman, R. Horizontal versus Vertical Charge and Energy Transfer in Hybrid Assemblies of Semiconductor Nanoparticles. *Beilstein J. Nanotechnol.* **2012**, *3*, 629–636.
- (14) Engelkes, V. B.; Beebe, J. M.; Frisbie, C. D. Length-Dependent Transport in Molecular Junctions Based on SAMs of Alkanethiols and Alkanedithiols: Effect of Metal Work Function and Applied Bias on Tunneling Efficiency and Contact Resistance. *J. Am. Chem. Soc.* **2004**, *126*, 14287–14296.
- (15) Holmlin, R. E.; Ismagilov, R. F.; Haag, R.; Mujica, V.; Ratner, M. A.; Rampi, M. A.; Whitesides, G. M. Correlating Electron Transport and Molecular Structure in Organic Thin Films. *Angew. Chem. Inter. Ed.* **2001**, *40*, 2316–2320.
- (16) Dayen, J.-F.; Devid, E.; Venkata Kamalakar, M.; Golubev, D.; Guédon, C.; Faramarzi, V.; Doudin, B.; van der Molen, S. J. Enhancing the Molecular Signature in Molecule-Nanoparticle Networks via Inelastic Cotunneling. *Adv. Mater.* **2013**, *25*, 400–404.
- (17) Beloborodov, S.; Lopatin, A. V.; Vinokur, V. M.; Efetov, K. B. Granular Electronic Systems. *Rev. Mod. Phys.* **2007**, *79*, 469–518.