

Delft University of Technology

Robust organic radical molecular junctions using acetylene terminated groups for c-au bond formation

Bejarano, Francesc; Olavarria-Contreras, Ignacio Jose; Droghetti, Andrea; Rungger, Ivan; Rudnev, Alexander; Gutiérrez, Diego; Mas-Torrent, Marta; Veciana, Jaume; Van Der Zant, Herre S.J.; Burzuri Linares, Enrique

DOI

10.1021/jacs.7b10019

Publication date 2018

Document Version Final published version

Published in Journal of the American Chemical Society

Citation (APA)

Bejarano, F., Ólavarria-Contreras, I. J., Droghetti, A., Rungger, I., Rudnev, A., Gutiérrez, D., Mas-Torrent, M., Veciana, J., Van Der Zant, H. S. J., Burzuri Linares, E., & More Authors (2018). Robust organic radical molecular junctions using acetylene terminated groups for c-au bond formation. *Journal of the American Chemical Society*, *140*(5), 1691-1696. https://doi.org/10.1021/jacs.7b10019

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

Green Open Access added to TU Delft Institutional Repository

'You share, we take care!' - Taverne project

https://www.openaccess.nl/en/you-share-we-take-care

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.

Article pubs.acs.org/JACS

Robust Organic Radical Molecular Junctions Using Acetylene Terminated Groups for C-Au Bond Formation

Francesc Bejarano,[†] Ignacio Jose Olavarria-Contreras,[‡] Andrea Droghetti,^{*,§} Ivan Rungger,^{||} Alexander Rudnev,^{⊥,#} Diego Gutiérrez,[†] Marta Mas-Torrent,[†] Jaume Veciana,[†][®] Herre S. J. van der Zant,[‡] Concepció Rovira,[†] Enrique Burzurí,^{*,‡,¶}[®] and Núria Crivillers^{*,†}[®]

[†]Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB- CSIC) and CIBER-BBN, Campus de la Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Spain

[‡]Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, Delft 2628 CJ, The Netherlands

[§]Nano-Bio Spectroscopy Group and European Theoretical Spectroscopy Facility (ETSF), Universidad del País Vasco (UPV/EHU), Avenida Tolosa 72, 20018 San Sebastian, Spain

^{II}National Physical Laboratory, Teddington TW11 0LW, United Kingdom

¹Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

[#]Russian Academy of Sciences A. N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninskii pr. 31, Moscow, 119991, Russia

[¶]IMDEA Nanoscience, Ciudad Universitaria de Cantoblanco, c/Faraday 9, 28049 Madrid, Spain

Supporting Information



ABSTRACT: Organic paramagnetic and electroactive molecules are attracting interest as core components of molecular electronic and spintronic devices. Currently, further progress is hindered by the modest stability and reproducibility of the molecule/electrode contact. We report the synthesis of a persistent organic radical bearing one and two terminal alkyne groups to form Au-C σ bonds. The formation and stability of self-assembled monolayers and the electron transport through singlemolecule junctions at room temperature have been studied. The combined analysis of both systems demonstrates that this linker forms a robust covalent bond with gold and a better-defined contact when compared to traditional sulfur-based linkers. Density functional theory and quantum transport calculations support the experimental observation highlighting a reduced variability of conductance values for the C-Au based junction. Our findings advance the quest for robustness and reproducibility of devices based on electroactive molecules.

1. INTRODUCTION

The molecule/electrode contact plays a fundamental role in the performance of molecular electronic devices since it directly affects the charge transport across the interface.¹⁻³ The search for a more stable molecule-electrode bond, a well-defined interface geometry, and more conductive interfaces is the driving force to pursue robust and efficient molecule based devices.⁴ The chemisorption of molecules on noble-metal electrodes has been mainly achieved through thiols,⁵ but also by employing other groups such as pyridines,⁶⁻⁹ amines,¹⁰⁻¹³ Nhetorocylic carbenes,¹⁴ isothiocyanide,¹⁵ and carbodithioate.¹⁶

Interestingly, some recent works have shown that the formation of covalent highly directional σ -bonded C-Au junctions provides high conductance at the single-molecule level. Different anchoring groups such as trimethyl tin (SnMe₃)terminated polymethylene chains¹⁷ and silyl-protected acetylenes^{18–20} have been employed for this aim. In the case of the silyl groups there is the need of applying in situ desilylation



Received: September 22, 2017 Published: January 7, 2018

chemistry to form the Au–C bond. On the contrary, the terminal acetylene (R—C \equiv C—H) group spontaneously forms stable C–Au bonds.^{21,22} This strategy has been mainly used to prepare self-assembled monolayers (SAMs) on Au (flat surfaces^{23–26} and Au nanoparticles²⁷) and on Ag.^{23,24} Charge transport measurements through some of these SAMs have been performed in large-area molecular junctions (using Ga₂O₃/E_{Galn} as top electrode), in an STM break-junction,²⁶ and with electrochemical scanning tunneling spectroscopy.²⁸ Recently, a mechanically controlled break-junction (MCBJ) technique was used to compare the single-molecule conductance of a family of alkynyl terminated oligophenylenes.²⁹ However, up to now, single-molecule measurements through bridges incorporating a functional moiety linked via a —C \equiv C—Au bond at room temperature (RT) are very scarce.

In the present work, we therefore aim at filling this fundamental knowledge gap. To this objective, we exploit the highly persistent perchlorotriphenylmethyl (PTM) radical as a functional moiety. We show that the $-C \equiv C$ —Au bond allows for drastic improvements in the reproducibility of conductance measurements and bond strength when compared to other commonly used contacts. We demonstrate that the magnetic character is preserved after covalent bonding. The charge transport mechanism of PTM radicals in the tunneling regime was previously addressed in SAMs covalently grafted to Au through a thiol group showing that the single-unoccupied molecular orbital (SUMO) was playing a crucial role in the transport enhancing the junction conductivity.³⁰⁻³² Electrochemical gating was also used to achieve a highly effective redox-mediated current enhancement.³³ Being all-organic, PTM radicals present an intrinsic magnetic moment, low spin-orbit coupling and low hyperfine interactions. These attractive redox and magnetic properties, absent in transitionmetal-based magnetic compounds, have recently attracted attention in molecular (spin)electronics,^{34–36} where long spin coherence times are required to preserve the information encoded in the electronic spin. The individual spin of different radical species has been detected in low-temperature electron transport measurements in the shape of Kondo correlations in molecular junctions^{37,38} and surfaces.^{39,40} The PTM radical has proved to be robust in the junction thanks to the encapsulation of the radical spin in a three chlorinated-phenyl shell. Moreover, it has been proved that the magnetic state of PTM-based polyradicals can be mechanically modified⁴¹ and electrically gated to form the basis of a quantum SWAP gate.⁴² Similar oligo(*p*-phenyleneethynylene) (OPE)-based radicals have shown large magneto-resistance effects that could be used to tune charge transport in metal-molecule junctions.⁴³ Moreover, although it remains still to be proved, organic radicals could act as spin filters⁴⁴ provided that a strong hybridization between spin and electrodes is achieved. Aside from the magnetic properties, the redox properties of similar organic radicals have been used to enhance charge transport in molecular junctions.⁴⁵ All these intriguing properties depend up to some extent on the reproducibility and strength of the bond radical to the electrodes, a key-step that we explore here.

Two novel PTM radical derivatives bearing one (1-Rad) and two (2-Rad) acetylene terminated groups (Figure 1a) have been designed and synthesized in order to form SAMs and single molecule junctions, respectively. Thanks to the stability of the alkynyl group, compared to the -SH one, there is no need of protecting and deprotecting it during the deprotonation and oxidation reactions required to generate the radical



Figure 1. (a) Chemical structure of the PTM radicals employed in this study. (b) Scheme of the SAM based on **1-Rad** (top) and MCBJ based on **2-Rad** (bottom).

species. Additionally, these linkers once formed are stable without showing signs of oxidation with time, as it is the case of most of the thiolated compounds.^{46–48} SAMs based on 1-Rad (Figure 1b) were successfully prepared. Several characterization techniques, electron paramagnetic resonance spectroscopy (EPR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry (CV), show the formation of a very stable metal-molecule covalent bond where the unpaired spin is preserved after bonding. We have further downscaled to the single-molecule level. Molecular junctions based on 2-Rad (Figure 1b) were prepared and compared with the equivalent bisthiophene-terminated derivative (3-Rad, Figure 1a) that shares the same functional core but is functionalized with thiophene anchoring groups.³⁷ Room temperature electron transport measurements and the statistical analysis show that 2-Rad form a very stable bond with a better defined anchoring geometry when compared to the S-Au bond in the 3-Rad, while still having similar current levels. These findings are supported by density functional theory (DFT) and quantum transport calculations that predict a C-Au bond three times stronger than the S-Au and with a lower anchoring geometry variability.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Self-Assembled Monolayers Preparation and Characterization. Molecules **1-Rad** and **2-Rad** were obtained through a two-step reaction from the hydrogenated precursors **1-H** and **2-H** involving the formation of a carbanion on the α carbon and the subsequent one-electron oxidation of this carbanion to its corresponding open-shell (radical) form (Scheme S1 in the Supporting Information (SI)). **1-H** and **2-H** were previously synthesized through a Horner–Wadsworth–Emmons reaction between the monophosphonate-PTM derivative (3)⁴⁹ and the bisphosphonate-PTM derivative (4),⁵⁰ respectively, and 4-ethylnylbenzaldehyde (Scheme S1). Closed- and open-shell molecules were fully characterized as described in the SI.

First, self-assembled monolayers (SAMs) of 1-Rad were prepared on Au(111) to investigate the formation of the C–Au bond. The SAM formation conditions were optimized to maximize the surface coverage (see the Supporting Information). SAMs were prepared under inert conditions to avoid the possible oxidation of the alkyne group in the presence of O_2 and Au, as previously reported.²⁵

At this point, it is worth mentioning the reactivity of the terminal acetylenes with the gold substrate. Maity et al. studied the functionalization of gold clusters with a series of terminal alkynes derivatives by means of various spectroscopic methods. They clearly demonstrated the binding motif and the loss of the terminal H through the heterolytic deprotonation of the alkyne as the key mechanism for the binding of the alkynyl group to gold.²² Furthermore, Raman spectroscopy has been used by several authors to identify the covalent C–Au formation.^{18,51,52} Taking all this into account, SAM-1-Rad was characterized by Raman spectroscopy (Figure 2a). The spectrum of the 1-Rad in



Figure 2. Characterization of SAM 1-Rad. (a) Raman spectrum of 1-Rad in powder (black) and SAM 1-Rad (blue). (b) High resolution Cl 2p XPS spectrum. (c) Cyclic voltammetry at different scans rates (100, 200, 400, 800, 1000 mV/s) and (d) EPR spectrum of a SAM 1-Rad.

powder was also acquired for comparison. The weak band corresponding to the C-C triple bond stretching is observed both in powder (2108 cm⁻¹) and red-shifted on surface (2035 cm^{-1}) confirming the integrity of the alkyne group after the monolayer formation. The displacement of the abovementioned band is in agreement with previous studies describing the reactivity of terminal alkynes on gold.²² Remarkable is the appearance of a new sharp band at 432 cm⁻¹ in the SAM spectrum. According to literature, ^{18,51,52} this band can be assigned to the characteristic C-Au stretching mode, and constitutes a strong proof of the covalent character of the binding between the PTM 1-Rad and the gold surface. These observations point to an up-right configuration of 1-Rad molecules maintaining the directional triple bond and losing a hydrogen atom. In addition, X-ray photoelectron spectra (XPS) confirmed the presence of chlorine (Figure 2b; see Figure S3 for the C 1s spectrum). The Cl 2p spectrum showed the typical doublet corresponding to Cl $2p_{1/2}$ and Cl $2p_{3/2}$ at 202.4 and 200.8 eV, respectively.

The contact angle value of the SAM **1-Rad** was found to be $79 \pm 4^{\circ}$, which is in agreement with previously reported PTM-terminated SAMs.^{53,54} Moreover, the multifunctional character of the PTM radical molecules allows using several techniques to confirm the successful grafting and the monolayer robustness. In the cyclic voltammetry, a single clearly reversible peak at -0.57 V (vs Fc⁺/Fc) can be observed for the SAM-**1-Rad** (Figure 2c), confirming the redox-active character of the monolayer. The observed peaks separation is attributed to lateral interactions between the electroactive PTM moieties.⁵⁴ As shown in Figure S2a, the current linearly increased with the scan rate, which is indicative of surface confined species. The surface coverage was found to be $8 \pm 1 \times 10^{-11} \text{ mol/cm}^2$ (see

the SI for further details on the calculation). The stability of the layer under electrochemical conditions was evaluated by performing 20 consecutive cycles while sweeping the bias between -1 and -0.2 V without showing a decrease of the current intensity in the redox peaks (Figure S2b). Finally, the paramagnetic character of the layer, and therefore the persistence of the unpaired spin in the **1-Rad** after covalent anchoring, was proved by EPR spectroscopy (Figure 2d). The signal can be fitted with a g value of 2.0024, in agreement with that obtained for PTM radical in solution, and a line width of 4.3 G. Thanks to the combination of these techniques, we clearly demonstrate that the redox-active **1-Rad** molecule covalently linked to the surface preserves the unpaired spin.

In addition to the chemical and structural characterization of the **1-Rad** SAMs, charge transport measurements across the monolayer were performed by top-contacting the layer with a ^EGaIn based electrode. Similar results to the ones previously reported with thiolated SAMs were obtained³² (see the SI for further details, Figure S4). The high reproducibility of these measurements supports the feasibility of the grafting approach to obtain stable monolayers through the C–Au bond.

2.2. Single-Molecule Junctions. We have further downscaled to study the bond and the conductance at the singlemolecule level. We have performed room temperature (RT) electron transport measurements through individual **2-Rad** molecules using the MCBJ technique described in refs 55 and 56 and in the SI. Figure 3a shows a two-dimensional



Figure 3. (a) Two-dimensional conductance vs electrode displacement histogram of the 2-Rad molecule constructed from 2500 consecutive traces at RT and 0.2 V bias voltage. The inset shows some selected individual traces. (b) One-dimensional conductance histogram for 2-Rad (top) and 3-Rad (bottom) constructed by integrating over the displacement in (a) and Figure S8b, respectively.

conductance vs electrode displacement histogram for **2-Rad** molecules. The histogram is made using 2500 consecutive traces recorded at an electrode speed of 6 nm/s and V = 0.2 V. Two characteristic features are present: first, the conductance drops exponentially from $10^{-4}G_0$ to the noise level for electrode displacements between 0 and 0.7 nm. These traces are typically attributed to empty junctions with no molecules bridging the electrodes. The second feature is a single flat plateau with a characteristic length of 2.3 nm (see length histogram in Figure S5) after which the conductance drops abruptly. Individual examples of these traces can be observed in the inset of Figure 3a. The plateau is indicative of the formation of a molecular

junction that breaks when the gap between the electrodes is too wide for the **2-Rad** molecule to bind. A significant 30% of the traces show molecular signatures. Interestingly, the plateau length plus the snap-back correction (\sim 0.5 nm) approximately matches the length of the relaxed **2-Rad** molecule bonded to Au (2.7 nm).

The conductance value of the plateau in Figure 3a is determined from the one-dimensional conductance histogram shown in Figure 3b. The dotted line is a log-normal distribution fit around the conductance regions displaying molecular features. The most probable conductance value for the **2-Rad** molecule is $8.8 \times 10^{-6}G_0$.

To gain a deeper insight, we have compared these results with the conductance characteristics of a similar PTM moiety functionalized with thiophene anchoring groups (3-Rad, Figure 1) measured with the scanning tunneling microscope (STM)based break-junction (STM-BJ) technique. This molecule was synthesized as previously reported.³⁷ As seen in Figure 3b (bottom), in the latter case, the conductance values appear more spread between two conductance plateaus at G_{high} = $10^{-4}G_0$ and $G_{low} = 4 \times 10^{-6}G_0$ (see also Figure S8). The asterisk indicates the noise level of the setup. The small spike at $\log(G/G_0) \sim -2.2$ in panel (b) bottom is an artifact related to the switching of the amplifier stage. This spread of values is signature of a weaker or ill-defined molecule-electrode contact⁵⁷ in contrast with the remarkably well-defined plateau measured in 2-Rad junctions, signature of a better-defined molecule-electrode anchoring geometry. Moreover, the size of the plateau (plus snap-back) in the 3-Rad junction extends only up to 0.95 nm, whereas the length of the fully stretched molecules is 1.7 nm, suggesting that the molecules are anchored adopting different electrode/molecule configurations (see length histograms of both species in the SI). These results point to a stronger mechanical bond in the case of 2-Rad that allows fully stretching of the molecule before breaking the junction and points to a preserved structural integrity of the molecule. Note that the strength in the mechanical bond is not straightforwardly translated into a higher conductance.

Finally, the only sensitive tool to detect the radical (unpaired) spin at the single molecule level is through its interaction with the conduction electrons in the shape of Kondo correlations.³⁷ These correlations are however only significant at very low temperatures for PTM radicals (<10 K).³⁷ Figure S6 shows some selected dI/dV curves measured at T = 4 K in a MCBJ setup. The current is measured at a fixed interelectrode distance and the differential conductance is thereafter numerically obtained. A zero-bias resonance is observed in some of the junctions. This resonance is typically associated with Kondo correlations in molecules or quantum dots containing magnetic impurities and appears when the electronic hybridization of impurity and conduction electrons is strong.

2.3. Theoretical Calculations. The strength of the mechanical bond between the molecule and Au is quantified by means of the maximum rupture force F and of the bond dissociation energy D.⁵⁸ These cannot be directly obtained from our experiments, but they can be estimated by calculating the potential energy surface (PES) for the stretched bond with DFT, and then fitting the PES with a Morse potential (details are given in the SI, Figures S11–S13).

We find that the C-Au bond forms at a bridge adsorption site, where F = 3.05 nN and D = 3.5 eV. The energy is about 300 meV lower than for the top adsorption site, while the hollow adsorption site is not stable as the geometry optimization ends up in the bridge configuration without going over any potential barrier. Most importantly, such a Au-C bond has to be elongated by about 0.5 Å under an applied force as large as 2.9 nN for the Au-C bond-breaking activation energy to equal RT (Figure S11). This means that in RT MCBJs experiments the Au-C bond will not break until it is stretched up to 0.5 Å. Overall the results support the observations about the mechanical junction stability in Figure 3. In contrast, as described in the SI, a thiophene linker establishes no covalent bond with a flat Au surface, so that it is physisorbed (Figures S9 and S10). A covalent bond can only be established between the thiophene S atom and an Au adatom on a corrugated surface (Figure S13). In this case, for the adatom-S bond, F and D are just 0.45 nN and 0.3 eV, respectively, and the bond-breaking activation energy equals RT when the bond is stretched by less than 0.1 Å. For comparison, we also point out that for the S-Au bond of standard thiol linkers used in previous experiments (Figure S12),³² F and D are about three times smaller than for the Au-C bond, i.e., F = 1.45 nN and D = 1.26 eV.

Finally, we also studied the conductance of junctions comprising 2-Rad and 3-Rad molecules by using DFT-based quantum transport calculations (details are given in the SI, and results in Figure 4). 3-Rad can contact either a rather flat part



Figure 4. (a) Transmission as a function of energy for different atomic configurations (CFGs): (b) CFG T1 and (c) CFG T2 are two typical structures expected to be found in high temperature break-junction measurements with **3-Rad** and Au; (d) with **2-Rad** directly bonded via C–Au link.

of the electrode or a protruding adatom, and we model these two situations by considering different atomic configurations (CFGs), for instance configuration CFG T1 and CFG T2 in Figure 4b,c. In the first case, as outlined above, the bond to the Au is noncovalent, and the molecule can therefore slide on the Au tip as the junction is elongated. The conductance is quite low due to the weak electronic coupling between Au and the

Journal of the American Chemical Society

molecule. For more corrugated Au tips, the covalent bond between the thiophene S atom and the protruding Au adatom results in an increased electronic coupling and therefore in a higher conductance. This is in agreement with the experimental results, where for **3-Rad** a quite wide range of conductances between a higher and a lower value is found (Figures 3b and S8).

For 2-Rad, whenever the relative displacement of the electrodes is in the plateau region of Figure 3, the linkers establish a strong covalent bond with the electrodes, where the C atom is on the bridge site between two Au atoms (Figure 4d), in an analogous way to what found for the adsorption on flat Au surfaces (see the SI). The fact that the molecule binds to the electrodes with such a locally well-defined C–Au bond, independently of the overall junction geometry, drastically reduces the variability in conductance values. The calculated transmission curve lies in an intermediate range between the ones for CFG T2 and CFG T1. The low bias conductance corresponds to the transmission at the Fermi energy, for which we obtain about 10^{-4} . This is on the upper end of the experimentally measured conductance peak (Figure 3).

3. CONCLUSIONS

In conclusion, the functionalization of a PTM organic radical with alkynyl end groups has led to the formation of a robust covalent binding between these electroactive and paramagnetic molecules and Au. Through a detailed comparison with a similar thiophene functionalized derivative, we prove that the Au–C bond provides a more robust and better-defined anchoring geometry as supported by DFT calculations. Our findings open the door to more reproducible spintronics devices based on multifunctional molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10019.

Synthesis of the compounds, SAM characterization, electron transport measurements on PTM-bis-thiophene, and details of the DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

*andrea.droghetti@ehu.eus *enrique.burzuri@imdea.org *ncrivillers@icmab.es

ORCID ©

Jaume Veciana: 0000-0003-1023-9923 Enrique Burzurí: 0000-0001-7906-7192 Núria Crivillers: 0000-0001-6538-2482

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge Dr. G. Sauthier from the ICN2 for the XPS measurements, Prof. Carlos Gomez from IcMOL for the SQUID measurements, A. Bernabé and Dr. V. Lloveras from ICMAB for the LDI-ToF and EPR measurements. This work was supported by FET ACMOL project (GA no. 618082), CIBER-BBN, the DGI (Spain) project FANCY CTQ2016-80030-R, the Generalitat de Catalunya (2014-SGR-17), and the

MINECO, through the "Severo Ochoa" Programme for Centers of Excellence in R&D (SEV-2015-0496). F.B. is enrolled in the Materials Science Ph.D. program of UAB. F.B. thanks the Ministerio de Educación, Cultura y Deporte for the FPU fellowship. We thank the Dutch science foundation NWO/FOM for financial support.

REFERENCES

(1) Zotti, L. A.; Kirchner, T.; Cuevas, J.; Pauly, F.; Huhn, T.; Scheer, E.; Erbe, A. *Small* **2010**, *6*, 1529–1535.

(2) Park, Y. S.; Whalley, A. C.; Kamenetska, M.; Steigerwald, M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L. *J. Am. Chem. Soc.* **2007**, *129*, 15768–15769.

(3) Seideman, T. Current-driven Phenomena in Nanoelectronics; Pan Stanford Publishing Pte. Ltd.: Singapore, 2011.

(4) Rudnev, A. V.; Kaliginedi, V.; Droghetti, A.; Ozawa, H.; Kuzume, A.; Haga, M.; Broekmann, P.; Rungger, I. *Sci. Adv.* 2017, *3*, e1602297.
(5) Huang, Z.; Chen, F.; Bennett, P. A.; Tao, N. J. Am. Chem. Soc.

2007, 129, 13225–13231. (6) Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. *Nat. Nanotechnol.* 2009, *4*, 230–234.

(7) Hong, W.; Manrique, D. Z.; Moreno-Garcia, P.; Gulcur, M.; Mishchenko, A.; Lambert, C. J.; Bryce, M. R.; Wandlowski, T. J. Am. Chem. Soc. **2012**, 134, 2292–2304.

(8) Kamenetska, M.; Quek, S. Y.; Whalley, A. C.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Nuckolls, C.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. J. Am. Chem. Soc. **2010**, 132, 6817–6821.

(9) Ma, Z.; Rissner, F.; Wang, L.; Heimel, G.; Li, Q.; Shuai, Z.; Zojer, E. Phys. Chem. Chem. Phys. **2011**, *13*, 9747–9760.

(10) Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904–907.

(11) Hybertsen, M. S.; Venkataraman, L.; Klare, J. E.; Whalley, A. C.; Steigerwald, M. L.; Nuckolls, C. J. Phys.: Condens. Matter 2008, 20, 374115–374128.

(12) Lu, Q.; Liu, K.; Zhang, H.; Du, Z.; Wang, X.; Wang, F. ACS Nano 2009, 3, 3861–3868.

(13) de la Llave, E.; Clarenc, R.; Schiffrin, D. J.; Williams, F. J. J. Phys. Chem. C 2014, 118, 468–475.

(14) Crudden, C. M.; Horton, J. H.; Ebralidze, I. I.; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H.-B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousina-Webb, A.; Wu, G. *Nat. Chem.* **2014**, *6*, 409–414.

(15) Ko, C.-H.; Huang, M.-J.; Fu, M.-D.; Chen, C. J. Am. Chem. Soc. 2010, 132, 756.

(16) Xing, Y.; Park, T.-H.; Venkatramani, R.; Keinan, S.; Beratan, D. N.; Therien, M. J.; Borguet, E. J. Am. Chem. Soc. **2010**, 132, 7946–7956.

(17) Cheng, Z.-L.; Skouta, R.; Vazquez, H.; Widawsky, J. R.; Schneebeli, S.; Chen, W.; Hybertsen, M. S.; Breslow, R.; Venkataraman, L. *Nat. Nanotechnol.* **2011**, *6*, 353-357.

(18) Hong, W.; Li, H.; Liu, S. X.; Fu, Y.; Li, J.; Kaliginedi, V.; Decurtins, S.; Wandlowski, T. J. Am. Chem. Soc. 2012, 134, 19425–19431.

(19) Huang, C.; Chen, S.; Baruël Ørnsø, K.; Reber, D.; Baghernejad, M.; Fu, Y.; Wandlowski, T.; Decurtins, S.; Hong, W.; Thygesen, K. S.; Liu, S.-X. Angew. Chem., Int. Ed. **2015**, *54*, 14304–14307.

(20) Fu, Y.; Chen, S.; Kuzume, A.; Rudnev, A.; Huang, C.; Kaliginedi, V.; Baghernejad, M.; Hong, W.; Wandlowski, T.; Decurtins, S.; Liu, S. *Nat. Commun.* **2015**, *6*, 6403–6410.

(21) Ford, M. J.; Hoft, R. C.; Mcdonagh, A. J. Phys. Chem. B 2005, 109, 20387–20392.

(22) Maity, P.; Takano, S.; Yamazoe, S.; Wakabayashi, T.; Tsukuda, T. J. Am. Chem. Soc. **2013**, 135, 9450–9457.

(23) Fracasso, D.; Kumar, S.; Rudolf, P.; Chiechi, R. C. RSC Adv. 2014, 4, 56026–56030.

Journal of the American Chemical Society

(24) Bowers, C. M.; Liao, K. C.; Zaba, T.; Rappoport, D.; Baghbanzadeh, M.; Breiten, B.; Krzykawska, A.; Cyganik, P.; Whitesides, G. M. ACS Nano **2015**, *9*, 1471–1477.

(25) Zaba, T.; Noworolska, A.; Bowers, C. M.; Breiten, B.; Whitesides, G. M.; Cyganik, P. J. Am. Chem. Soc. 2014, 136, 11918– 11921.

(26) Pla-Vilanova, P.; Aragonès, A. C. A. C.; Ciampi, S.; Sanz, F.; Darwish, N.; Diez-Perez, I. *Nanotechnology* **2015**, *26*, 381001–381007.

(27) Zhang, S.; Chandra, K. L.; Gorman, C. B. J. Am. Chem. Soc. 2007, 129, 4876–4877.

(28) Ricci, A. M.; Calvo, E. J.; Martin, S.; Nichols, R. J. J. Am. Chem. Soc. 2010, 132, 2494–2495.

(29) Olavarria-Contreras, I. J.; Perrin, M. L.; Chen, Z.; Klyatskaya, S.; Ruben, M.; van der Zant, H. S. J. *J. Am. Chem. Soc.* **2016**, *138*, 8465–8469.

(30) Souto, M.; Yuan, L.; Morales, D. C.; Jiang, L.; Ratera, I.; Nijhuis, C.; Veciana, J. J. Am. Chem. Soc. 2017, 139, 4262–4265.

(31) Crivillers, N.; Munuera, C.; Mas-Torrent, M.; Simão, C.; Bromley, S. T.; Ocal, C.; Rovira, C.; Veciana, J. *Adv. Mater.* **2009**, *21*, 1177–1181.

(32) Yuan, L.; Franco, C.; Crivillers, N.; Mas-Torrent, M.; Cao, L.; Sangeeth, C. S. S.; Rovira, C.; Veciana, J.; Nijhuis, C. A. *Nat. Commun.* **2016**, *7*, 12066–12076.

(33) Rudnev, A. V.; Franco, C.; Crivillers, N.; Seber, G.; Droghetti, A.; Rungger, I.; Pobelov, I. V.; Veciana, J.; Mas-Torrent, M.; Rovira, C. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27733–27737.

(34) Ratera, I.; Veciana, J. Chem. Soc. Rev. 2012, 41, 303-349.

(35) Mas-Torrent, M.; Crivillers, N.; Mugnaini, V.; Ratera, I.; Rovira, C.; Veciana, J. J. Mater. Chem. **2009**, *19*, 1691–1695.

(36) Mas-Torrent, M.; Crivillers, N.; Rovira, C.; Veciana, J. Chem. Rev. 2012, 112, 2506–2527.

(37) Frisenda, R.; Gaudenzi, R.; Franco, C.; Mas-Torrent, M.; Rovira,

C.; Veciana, J.; Alcon, I.; Bromley, S. T.; Burzurí, E.; Van Der Zant, H. S. J. Nano Lett. **2015**, *15*, 3109–3114.

(38) Zhang, Y.; Kahle, S.; Herden, T.; Stroh, C.; Mayor, M.; Schlickum, U.; Ternes, M.; Wahl, P.; Kern, K. *Nat. Commun.* **2013**, *4*, 2110–2115.

(39) Liu, J.; Isshiki, H.; Katoh, K.; Morita, T.; Breedlove, B. K.; Yamashita, M.; Komeda, T. J. Am. Chem. Soc. **2013**, 135, 651–658.

(40) Müllegger, S.; Rashidi, M.; Fattinger, M.; Koch, R. J. Phys. Chem. C 2013, 117, 5718–5721.

(41) Gaudenzi, R.; Burzurí, E.; Reta, D.; Moreira, I. de P. R.; Bromley, S. T.; Rovira, C.; Veciana, J.; van der Zant, H. S. J. *Nano Lett.* **2016**, *16*, 2066–2071.

(42) Gaudenzi, R.; de Bruijckere, J.; Reta, D.; Moreira, I. de P. R.; Rovira, C.; Veciana, J.; van der Zant, H. S. J.; Burzurí, E. *ACS Nano* **2017**, *11*, 5879–5883.

(43) Hayakawa, R.; Karimi, M. A.; Wolf, J.; Huhn, T.; Zollner, M. S.; Herrmann, C.; Scheer, E. *Nano Lett.* **2016**, *16*, 4960–4967.

(44) Herrmann, C.; Solomon, G. C.; Ratner, M. A. J. Am. Chem. Soc. 2010, 132, 3682–3684.

(45) Liu, J.; Zhao, X.; Al-Galiby, Q.; Huang, X.; Zheng, J.; Li, R.; Huang, C.; Yang, Y.; Shi, J.; Manrique, D. Z.; Lambert, C. J.; Bryce, M. R.; Hong, W. *Angew. Chem., Int. Ed.* **2017**, *56*, 13061–13065.

(46) Srisombat, L.; Jamison, A. C.; Lee, T. R. Colloids Surf., A 2011, 390, 1–19.

(47) Tarlov, M. J.; Newman, J. G. Langmuir 1992, 8, 1398-1405.

(48) Scott, J. R.; Baker, L. S.; Everett, W. R.; Wilkins, C. L.; Fritsch, I. Anal. Chem. **1997**, 69, 2636–2639.

(49) Rovira, C.; Ruiz-Molina, D.; Elsner, O.; Vidal-gancedo, J.; Bonvoisin, J.; Launay, J.; Veciana, J. *Chem. - Eur. J.* **2001**, *7*, 240–250.

(50) Reitzenstein, D.; Quast, T.; Kanal, F.; Kullmann, M.; Ruetzel, S.; Hammer, M. S.; Deibel, C.; Dyakonov, V.; Brixner, T.; Lambert, C. *Chem. Mater.* **2010**, *22*, 6641–6655.

(51) Osorio, H. M.; Cea, P.; Ballesteros, L. M.; Gascón, I.; Marques-Gonzalez, S.; Nichols, R. J.; Pérez-Murano, F.; Low, P.; Martin, S. J. Mater. Chem. C 2014, 2, 7348–7355.

(52) Laurentius, L.; Stoyanov, S. R.; Gusarov, S.; Kovalenko, A.; Du, R.; Lopinski, G. P.; Mcdermott, M. T. ACS Nano 2011, 5, 4219–4227.

(53) Simão, C.; Mas-Torrent, M.; Veciana, J.; Rovira, C. *Nano Lett.* **2011**, *11*, 4382–4385.

- (54) Crivillers, N.; Mas-Torrent, M.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. J. Am. Chem. Soc. **2008**, 130, 5499–5506.
- (55) Martin, C. A.; Smit, R. H. M.; Egmond, R.; van der Zant, H. S. J.; van Ruitenbeek, J. M. *Rev. Sci. Instrum.* **2011**, *82*, 053907.
- (56) Perrin, M. L.; Burzurí, E.; van der Zant, H. S. J. Chem. Soc. Rev. 2015, 44, 902-919.

(57) Etcheverry-Berríos, A.; Olavarría, I.; Perrin, M. L.; Díaz-Torres, R.; Jullian, D.; Ponce, I.; Zagal, J. H.; Pavez, J.; Vásquez, S. O.; van der Zant, H. S. J.; Dulić, D.; Aliaga-Alcalde, N.; Soler, M. *Chem. - Eur. J.* **2016**, *22*, 12808–12818.

(58) Grandbois, M.; Beyer, M.; Rief, M.; Clausen-Schaumann, H.; Gaub, H. E. *Science* **1999**, *283*, 1727–1730.