

Conductive Molecular Silicon

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Conductive Molecular Silicon

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Supporting Information Placeholder

ABSTRACT: Bulk silicon, the bedrock of information technology, consists of the deceptively simple electronic structure of just Si–Si σ bonds. Diamond has the same lattice structure as silicon, yet the two materials have dramatically different electronic properties. Here, we report the specific synthesis and electrical characterization of a class of molecules, oligosilanes, that contain strongly interacting Si–Si σ bonds, the essential components of the bulk semiconductor. We use the scanning tunneling microscope based break-junction technique to compare the single molecule conductance of these oligosilanes to alkanes. We find that the molecular conductance decreases exponentially with increasing chain length with a decay constant $\beta = 0.27 \pm 0.01 / \text{\AA}$, comparable to that of a conjugated chain of C=C π -bonds. This result demonstrates the profound implications that sigma conjugation has on the conductivity of silicon.

Bulk silicon exclusively contains Si–Si σ bonds; indeed, the material can be imagined as a series of one-dimensional chains of Si-atoms cross-linked in three dimensions. It was first shown in the mid-twentieth century that short chains of Si atoms (oligosilanes) have markedly differently electronic properties relative to their structural analogs, the alkanes.¹ While alkanes do not absorb light above 190 nm, Gilman et al. observed that permethyloligosilanes (e.g. hexamethyldisilane and higher oligomers) display strong absorbance in the range of 200–300 nm.² In a trend similar to linearly conjugated systems such as oligoenes,³ the position of maximum absorbance (λ_{max}) and absorption coefficient (ϵ) increases with the length of the Si chain.^{2,4} This observation led to speculation that saturated oligosilanes may undergo electron transfer chemistry similar to conjugated carbon-based materials. Indeed, the pioneering work of West established that the stable delocalized decamethylcyclopentasilane radical anion can be observed by EPR spectroscopy⁵ and that linear and cyclic oligosilanes form charge transfer complexes with π -acceptors such as tetracyanoethylene (TCNE).⁶

These promising initial experiments inspired considerable interest in the development of polymeric silanes as electronic materials; however, the challenges in silane synthesis ultimately hindered the widespread study of oligo- and polysilanes after the 1980's.^{7,8,9} High molecular weight polymers are obtained via sodium-mediated Wurtz-type coupling of dichlorosilane monomers. The harsh conditions limit the

functional group tolerance to relatively inert alkyl and aryl substituents¹⁰ and the resultant polymers also suffer from low yields and/or wide molecular weight distributions.¹¹ Herein, we report the synthesis of oligomeric silanes of specific length functionalized with anchor groups, which enable single molecule conductance measurements. We carry out these conductance measurements on a set of SiMe₂ oligomers that are terminated with 4-(methylthio)phenyl groups (Figure 1), which bind to undercoordinated Au to form single molecule junctions with linear silane backbones that are stable under ambient conditions.^{12,13}

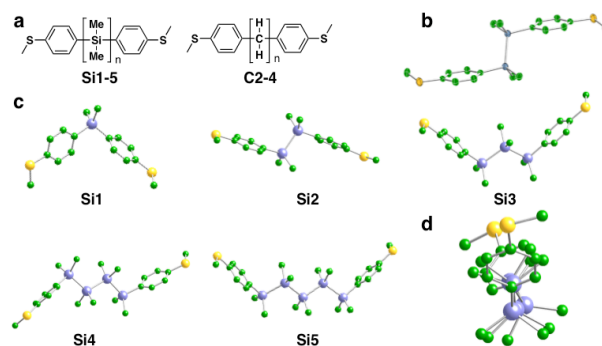
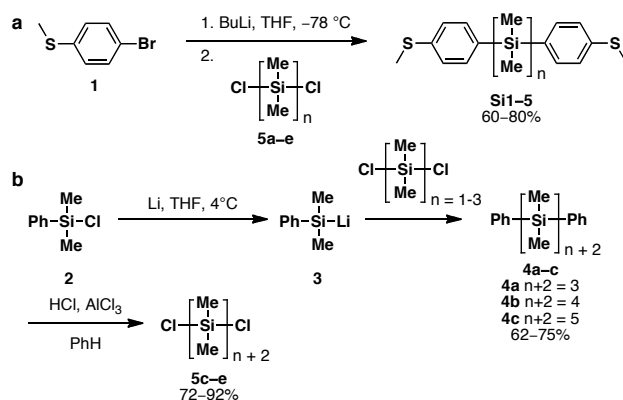


Figure 1. a) Molecular structure of methyl sulfide-capped oligosilanes **Si1–5** and alkanes **C2–4**. b) ORTEP of a single molecule of silane **Si2**. Ellipsoids are shown at the 50% probability level. Hydrogens omitted for clarity: sulfur, yellow; silicon, blue; carbon, green. c) Calculated lowest energy structure of oligosilanes **Si1–5**. Hydrogens omitted for clarity: sulfur, yellow; silicon, blue; carbon, green. B3LYP/6-31G**. d) Perspective drawing of lowest energy conformation of pentasilane **Si5** demonstrating flexible silicon backbone.

We synthesize the oligomeric materials via silylation of an aryllithium reagent with a symmetric α,ω -dichlorooligosilane (**5a–e**) (Scheme 1A). α,ω -Dichlorooligosilanes are a known class of molecules and are typically synthesized by chlorination of dodecamethylcyclohexasilane.¹⁴ This method yields a complex mixture of chlorosilanes that we found cumbersome. Instead, we employed an iterative synthesis (Scheme 1B) of the α,ω -dichlorooligosilanes **5c–e** in which dimethylphenylsilyl lithium (**3**)¹⁵ is coupled to commercially available dichlorodimethylsilane (**5a**) or dichlorotetramethyldisilane (**5b**) to yield α,ω -diphenyloligosilanes **4a–b**. Protodesilylation with HCl/AlCl₃ yields α,ω -dichlorooligosilanes **5c–d** that can

then be coupled with the aryl lithiates or with silyl lithium **3** to yield pentasilane **4c**.¹⁶ The aryl silylation reaction efficiently yields the bis(4-(methylthio)phenyl)silanes in 60–80% yield. These compounds are air-stable solids that are soluble in common organic solvents including hydrocarbon, aromatic, and chlorinated solvents. The crystal structure of disilane **Si2** (Figure 1B) confirms that the Si-chain adopts a fully staggered *trans* conformation, which is expected to have the optimal orbital overlap for electronic communication.^{17,18} It is also important to note that there is no detectable decomposition or oxidation during the break junction measurements.

Scheme 1. Synthetic scheme for α,ω -bis(4-methylthio)phenyloligosilanes **Si1–5. a) Aryl silylation reaction. b) Synthesis of α,ω -dichlorooligosilanes **5c–e**.**



The conductance of these oligosilanes **Si1–5** is measured using a scanning tunneling microscope-based break-junction (STM-BJ) technique.^{12,19} This is carried out using a gold tip and substrate to repeatedly form and break gold point contacts in solutions of the target compounds (1 mM) in 1,2,4-trichlorobenzene. The conductance (current/voltage) is measured across the Au tip/substrate pair as a function of the tip/substrate separation. The conductance traces show plateaus at integer multiples of G_0 , the quantum of conductance, which correspond to multiples of Au atoms. At a conductance value below G_0 , a molecule-dependent plateau is observed (Inset, Figure 2A). Thousands of traces are measured and used to generate two-dimensional conductance-displacement histograms without data selection.^{20,21} Figure 2A shows such a 2D-histogram measured with **Si1** generated with 27,000 traces (two-dimensional histograms for other compounds are shown in the SI). We see an intense peak around $10^{-4} G_0$, which extends approximately 0.5 nm indicating that single molecule junctions are formed reproducibly with this molecule and can be elongated over that distance.

One-dimensional conductance histograms generated using logarithm bins for the five silanes studied are shown in Figure 2B. A broad peak in the histograms at a molecule dependent conductance value is observed (black arrows). The peak broadness is attributed to conductance variation from junction to junction primarily due to variations in the Au-S-C torsional angle.^{22,23} The peak positions are plotted in Figure 2C on a semi-log scale against the length of the silane (the distance between the carbons para to the methylthio substituent). We see that the conductance decreases exponentially with increasing length for the first four silanes in

this series, i.e. $G \sim e^{-\beta L}$ with a $\beta = 0.27 \pm 0.01 \text{ \AA}^{-1}$.²⁴ The decay constant measured here is different than the value ($\beta = 0.16 \text{ \AA}^{-1}$) measured in a study of photoinduced electron transfer in porphyrin-silane-fullerene dyads.²⁵ Excited state relaxation and low-bias molecular conduction are fundamentally different processes. This β -value compares favorably to β -values observed for conjugated olefins, which range from $0.17\text{--}0.27 \text{ \AA}^{-1}$.^{23,26} The statistically determined conductance of the pentasilane **Si5** falls below this line, as can be seen in Figure 3C. We attribute this small decrease in conductance of **Si5** to its slightly twisted backbone structure,²⁷ as determined from DFT calculations (Figure 1D), which decreases the “conjugation” of this molecule, similar to gauche defects in alkane backbones.²⁸ Notably, the difference in through-space length between *trans*-**Si5** and the twisted conformer shown in Fig 1D is insignificant.

In addition to a strong molecule-dependent peak, Figure 2B shows that all these histograms have a less intense peak at approximately $10^{-3} G_0$ (blue arrow, Figure 2A and B). The two-dimensional histogram indicates this peak corresponds to conductance features that occur immediately after the single atom contact is broken at a short tip/sample displacement. Although the origin of this high-conductance feature is not fully understood, control experiments with molecules with only one terminal methylsulfide or no anchor groups were conducted to test if the molecule interacts with gold through the Si-backbone, in analogy with an oligoene potentiometer.²³ Neither molecule showed clear conductance signatures (see SI for synthesis and conductance histograms), demonstrating that in fact both sulfides are required for junction formation. Another possibility is that at a short electrode displacement a *cis*-conformation of the molecule in which the thioanisole moieties stack could be formed, leading to a higher conductance with a short molecular plateau length. In support of this hypothesis, we offer that conductance through the π - π stack in cyclophanes has been recently reported²⁹ and that this hypothesis accounts for the observation of the same $10^{-3} G_0$ peak in an analogous alkane series (vide infra).

These conductance results confirm the prediction first advanced several decades ago that while silanes are structural analogs of alkanes, their electronic properties are far more similar to conjugated, unsaturated hydrocarbons.¹ The conductance of oligosilanes **Si1–5** compared to alkanes **C2–4** inspired us to investigate electronic communication between terminal sulfur atoms in these molecules. We conducted density functional theory (DFT) based calculations (B3LYP/6-31G**) on **Si1–Si5**. We found in each case that the HOMO is distributed evenly across the silicon chain, the π systems of the arenes and the p- π orbitals of the two sulfur atoms.³⁰ The HOMO of **Si4** is depicted as a representative example in Figure 3. The contrast with the carbon analog **C4** is dramatic: there is essentially no electron density along the C-C backbone and the HOMO is localized exclusively on the thioanisole fragments. In contrast, the HOMO of a butadiene terminated with 4-(methylthio)phenyl groups (**6**) is fully delocalized, as in the silane, indicating that the two sulfur p- π orbitals couple much more strongly across the Si-Si and C=C bonds than the C-C bond.

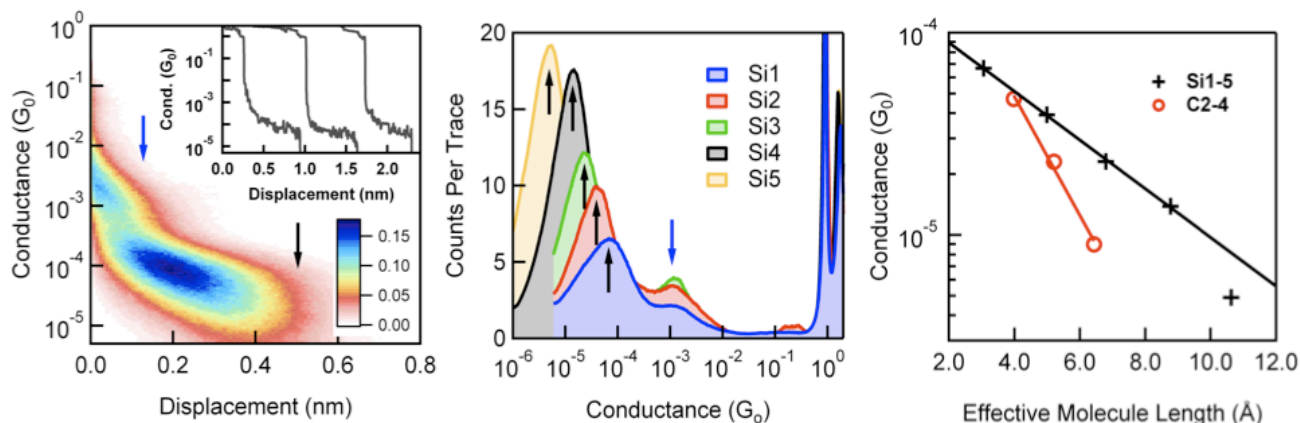


Figure 2. (a) Two-dimensional conductance histogram for **Si1** showing a clear conductance peak that extends over a distance of 0.5 nm relative to the break of the G_0 contact. The inset shows individual conductance traces. (b) Logarithm-binned conductance histograms generated using a bin size of 100/decade for compounds **Si1-Si5**. (c) Conductance peak values of the single molecule junctions with **Si n** (black) and **C n** (red) series as a function of the effective molecular length (L) in Ångstroms. L is defined as the distance between the carbons para to the methylthio substituent. L was determined from crystal structures as well as using Chem3D and DFT calculations. The values thus obtained vary insignificantly (<3%). The measured decay constant β is $0.27 \pm 0.01 / \text{Å}$ (**Si n** , black) and $0.68 \pm 0.05 / \text{Å}$ (**C n** , red).

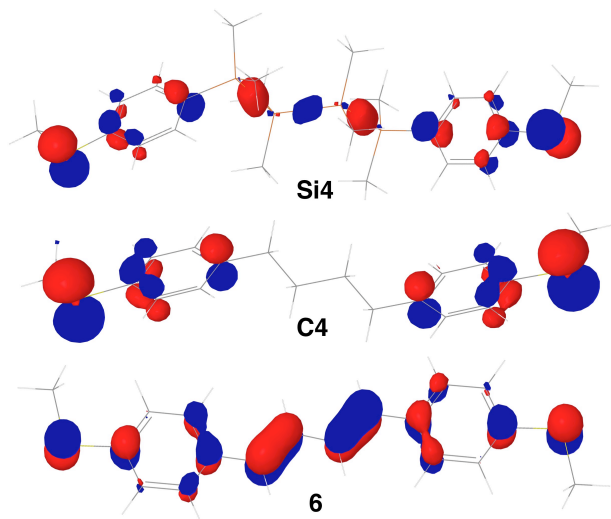


Figure 3. Calculated HOMO's of a) tetrasilane **Si4**, b) butane **C4**, and c) 1,4-bis(4-(methylthio)phenyl)buta-1,3-diene **6**. B3LYP/6-31G** level of theory.

To elucidate the greater coupling observed in the Si-Si and C=C materials, we separated the molecular conductors into their constituent components: the 4-(methylthio)phenyl end groups and conducting oligomer.^{31,32} Computational analysis of each part was conducted (see SI, Table S3). We find that the HOMOs of tetrasilane and butadiene are delocalized over the respective C and Si atoms. The HOMO level of 4-methylthioanisole lies at -5.49 eV with respect to vacuum, and it is a close combination of the p- π lone pair on S and the π -space on the ring. We find that of the three oligomers investigated, the tetrasilane (HOMO = -5.96 eV) and butadiene (HOMO = -5.60 eV) lie closest in energy to that of the 4-methylthioanisole, suggesting that extensive mixing of the thioanisole and Si-Si orbitals ($\sigma(\text{Si-Si})-\pi$ conjugation) is occurring; moreover, Figure 3 demonstrates that the orbital mixing is geometrically accessible.³³ The HOMO of hexane

lies at the substantially lower energy of -8.29 eV, resulting in very minimal mixing of the σ -framework and thioanisole orbitals (negligible $\sigma(\text{C-C})-\pi$ conjugation). As a result, the HOMO of **C4** is localized on the thioanisole. Our results indicate that uniform delocalization of the HOMO over the entire molecule improves conductance. Consistent with this observation, a siloxane variant of **Si2** was synthesized in which the Si chain is disrupted with an O atom; no conductance peak was observed (see SI for synthesis, conductance histogram and HOMO calculation). We also note in passing that differential orbital coupling may account for the difference in contact resistance observed for alkanes and oligosilanes as seen in Figure 2C.

We present a quantitative comparison of the conductive properties of oligosilanes and alkanes which is enabled by straightforward synthetic access to silanes functionalized with aurophilic contact groups. We have found that saturated Si nanowires display very slow decay of conductance with length; the decay constant is comparable to the decay constant of polyacetylene fragments (oligoenes) and is considerably less than alkane structural analogs. These results, coupled to our theoretical studies, highlight the important role of σ -bond conjugation in charge transport through Si-Si σ bonds. Currently the application of Si oligomers and polymers in electronic devices is limited,⁸ while applications of conjugated carbon-based materials such as polyacetylene are ubiquitous.³⁴ The materials described herein have promising physical properties which are complementary to those of rigid, conjugated systems, including conformational flexibility, air and thermal stability, as well as high solubility in common organic solvents. We expect that the desirable physical properties and high conductance of the materials described herein will result in the development of novel molecular devices and nanoscale architectures.

ASSOCIATED CONTENT

Supporting information. Synthetic methods and procedures, characterization data, electrochemical and spectroscopic charac-

1 terization, computational data, and crystallographic data. The
2 information is available free of charge via the Internet at
3 <http://pubs.acs.org>.

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24 ABBREVIATIONS

25 DFT, density functional theory; HOMO, highest occupied mo-
26 lecular orbital; Me, methyl; mM, millimolar; ORTEP, Oak
27 Ridge Thermal Ellipsoid Plot program; SI, supporting infor-
28 mation; STM-BJ, scanning tunneling microscope break-
29 junction.

30 REFERENCES

- 31 (1) West, R.; Carberry, E. *Science* **1975**, *189*, 179.
32 (2) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet.*
33 *Chem.* **1964**, *2*, 369.
34 (3) Hausser, K. W.; Kuhn, R.; Smakula, A.; Hoffer, M. *Z. Phys.*
35 *Chem. B-Chem. E.* **1935**, *29*, 371.
36 (4) Gilman, H.; Morris, P. J. *J. Organomet. Chem.* **1966**, *6*, 102.
37 (5) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**,
38 *91*, 5446.
39 (6) Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824.
40 (7) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
41 (8) Feigl, A.; Bockholt, A.; Weis, J.; Rieger, B. *Adv. Polym. Sci.*
42 **2011**, *235*, 1.
43 (9) David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K.
44 S. V. *J. Am. Chem. Soc.* **1981**, *103*, 7352.
45 (10) Jones, R. G. Holder, S. J. *Polym. Int.* **2006**, *55*, 711.
46 (11) Benfield, R. E.; Cragg, R. H.; Swain, A. C. *J. Chem. Soc.*
47 *Chem. Comm.* **1992**, 112.

(12) a) Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen,
M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904. b) 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.

(13) Xu, B. Q.; Tao, N. J. *J. Science* **2003**, *301*, 1221.

(14) a) Sen, P. K.; Ballard, D.; Gilman, H. *J. Organomet. Chem.*
1968, *15*, 237. b) Chernyavskii, A. I., Yu, D., Larkin, D. Y.,
Chernyavskaya, N. A. *J. Organomet. Chem.* **2003**, *679*, 17. c) Gil-
man, H., Inoue, S. *J. Org. Chem.* **1964**, *29*, 3418.

(15) a) George, M. V., Peterson, D. J., Gilman, H. *J. Am. Chem.*
Soc. **1960**, *82*, 403. b) Fleming, I.; Roberts, R. S.; Smith, S. C. *J.*
Chem. Soc. Perk. T. I **1998**, 1209. c) Shibano, Y.; Sasaki, M.; Tsuji,
H.; Araki, Y.; Ito, O.; Tamao, K. *J. Organomet. Chem.* **2007**, *692*,
356.

(16) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.;
Sanderson, P. E. J. *J. Chem. Soc. Perk. T. I* **1995**, 317.

(17) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi,
S.; Toshimitsu, A. *Angew. Chem. Int. Edit.* **2000**, *39*, 3287.

(18) George, C. B.; Ratner, M. A.; Lambert, J. B. *J. Phys. Chem.*
A **2009**, *113*, 3876.

(19) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.;
Hybertsen, M. S.; Steigerwald, M. L. *Nano. Lett.* **2006**, *6*, 458.

(20) Martin, C. A.; Ding, D.; Sorensen, J. K.; Bjornholm, T.; van
Ruitenbeek, J. M.; van der Zant, H. S. J. *J. Am. Chem. Soc.* **2008**,
130, 13198.

(21) 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.

(22) Park, Y. S.; Widawsky, J. R.; Kamenetska, M.; Steigerwald,
M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L. *J. Am.*
Chem. Soc. **2009**, *131*, 10820.

(23) Meisner, J. S.; Kamenetska, M.; Krikorian, M.; Steigerwald,
M. L.; Venkataraman, L.; Nuckolls, C. *Nano. Lett.* **2011**, *11*, 1575.

(24) a) Griffiths, D. J. *Introduction to Quantum Mechanics*, 2nd
ed. Ch. 8 (Pearson Prentice Hall, Upper Saddle River, New Jersey,
2005). b) Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.;
Engelkes, V. B.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1881.

(25) Sasaki, M.; Shibano, Y.; Tsuji, H.; Araki, Y.; Tamao, K.;
Ito, O. *J. Phys. Chem. A* **2007**, *111*, 2973.

(26) Visoly-Fisher, I.; Daie, K.; Terazono, Y.; Herrero, C.;
Fungo, F.; Otero, L.; Durantini, E.; Silber, J. J.; Sereno, L.; Gust,
D.; Moore, T. A.; Moore, A. L.; Lindsay, S. M. *P. Natl. Acad. Sci.*
USA **2006**, *103*, 8686.

(27) a) Albinsson, B.; Antic, D.; Neumann, F.; Michl, J. *J. Phys.*
Chem. A **1999**, *103*, 2184. b) Schepers, T.; Michl, J. *J. Phys. Org.*
Chem **2002**, *15*, 490.

(28) Jones, D. R.; Troisi, A. *J. Phys. Chem. C* **2007**, *111*, 14567.

(29) Schneebeli, S. T.; Kamenetska, M.; Cheng, Z. L.; Skouta,
R.; Friesner, R. A.; Venkataraman, L.; Breslow, R. *J. Am. Chem.*
Soc. **2011**, *133*, 2136.

(30) Pitt, C. G.; Bock, H. *J. Chem. Soc. Chem. Comm.* **1972**, 28.

(31) Bock, H.; Ensslin, W. *Angew. Chem. Int. Ed.* **1971**, *10*, 404.

(32) Schepers, T.; Michl, J. *J. Phys. Org. Chem.* **2002**, *15*, 490.

(33) Pitt, C. G.; Toren, E. C.; Carey, R. N. *J. Am. Chem. Soc.*
1972, *94*, 3806.

(34) Heeger, A. J. *Chem. Soc. Rev.* **2010**, *39*, 2354.

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