JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Chloride Surface Terminated Silicon Nanocrystal Mediated Synthesis of Poly(3-hexylthiophene)

Muhammad Amirul Islam, Tapas K. Purkait, and Jonathan G. C. Veinot*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

ABSTRACT: Abundant and environmentally benign metal-free silicon-based reagents, including chloride surface-terminated silicon nanocrystals (Cl-SiNCs) and silicon wafers as well as molecular chlorosilanes, were explored as catalysts for the synthesis of poly-3-hexylthiophene (P3HT) at room temperature. Cl-SiNC catalysts exhibit the highest activity of those investigated, and systems based upon single-crystal silicon wafers provide convenient, straightforward purification. The as-prepared P3HT exhibits moderate molecular weights and bears H/Br or Br/Br end groups; these properties will allow direct application and also facilitate their use as macroinitiators in the syntheses of block and/or telechelic polymers. The silicon-based systems are expected to provide an efficient metal-free catalytic preparation of functional polymers.

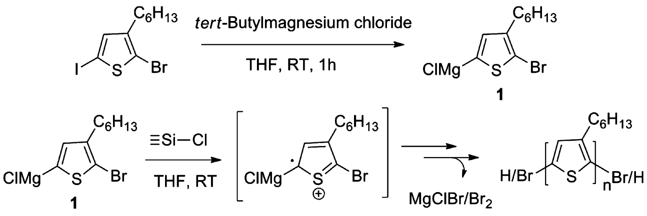
Conjugated polymers hold substantial potential for applications in optoelectronic devices and flexible electronics, partly because of their low cost, favorable mechanical properties, structural tailorability, solution processability, and straightforward device fabrication.[1] Poly(3-alkylthiophenes) and their derivatives have been studied extensively as active materials in bulk-heterojunction solar cells, light-emitting diodes, organic thin-film transistors, and sensors.[1−4] In this context, it is reasonable to classify it as a workhorse material in organic electronics. Common synthetic methods employed to prepare poly- and oligothiophenes include electropolymerization,[5] transition-metal-catalyzed coupling,[6−12] and oxidative polymerization.[13,14] Electropolymerization usually provides insoluble products.[14] Metal-catalyzed oxidative polymerization typically employs Lewis acidic centers that induce reaction. For example, ferric chloride is believed to initiate polymerization via single-electron oxidation of thiophene.[13] Other examples of Lewis acid-mediated processes employ $AlCl_3$ or BF_3 to decrease the aromaticity of the thiophene ring and lower its oxidation potential; this activation allows the preparation of high-quality films by subsequent electrooxidative polymerization.[15]

Despite allowing access to high-quality materials, metal-based catalysts can dramatically impact device performance. Even trace transition-metal impurities can limit the optoelectronic properties of these attractive materials.[16] It is also reasonable that transition-metal impurities can shorten device lifetimes by inducing degradation of the polymer. In this context, troublesome and costly purification steps are often essential. Clearly, a convenient metal-free synthesis of poly- and oligothiophenes and similar polymers would be extremely attractive, but few examples exist.[17]

Silicon tetrachloride is a weak Lewis acid that can form hypervalent species in the presence of Lewis bases.[18,19] Chloride-terminated silicon nanocrystals (Cl-SiNCs) can be prepared using a variety of protocols.[20−23] Wheeler et al.[23] reported that Cl surface termination can lead to a Lewis acidic NC surface. It has been proposed that in these nanosystems electron density is drawn from surface atoms, which lowers the lowest unoccupied molecular orbital (LUMO). This process facilitates transfer of electron density from donor molecules to the SiNC. This results in a weakening of surface Si−Cl bonds as well as lengthening/weakening of the donor molecule bonds through hypervalent bond formation. In this regard, Cl-SiNCs offer an attractive metal-free reactive species that could be exploited as a catalyst for the preparation of poly- and oligothiophene derivatives.

Given that single-electron transfer (SET) reactions are well-known for Grignard reagents[24] and oxidative homocoupling of Grignard reagents is promoted by Lewis acidic iron(III) catalysts,[25] we chose to investigate the reactivity of 5-chloromagnesio-2-bromo-3-hexylthiophene (**1**) with Cl-SiNCs, Cl-terminated silicon wafers (Cl-SiWFs), and molecular chlorosilanes in the preparation of poly-3-hexylthiophene (P3HT). The general synthetic approach is summarized in Scheme 1, where SET from Grignard monomer **1** to the Cl-SiNC LUMO forms the radical cation intermediate shown, which induces polymer formation.

Scheme 1. Two-Step Synthesis of P3HT



Cl-SiNCs were prepared via PCl_5-induced chlorination of hydride surface-terminated silicon nanocrystals (H-SiNCs) obtained from a well-established method involving thermal treatment of commercial hydrogen silsesquioxane developed in our laboratory.[22,26] The average diameter of the Cl-SiNCs (3.2 ± 0.65 nm) was determined using transmission electron

Received: July 24, 2014
Published: October 10, 2014

microscopy (TEM) (Figure 1a). The chloride surface termination of SiNCs is evidenced by the evolution of the FTIR spectra (Figure 1b). The Si−H absorption at 2068 cm^{-1} characteristic of H-SiNCs is replaced by a characteristic Si−Cl absorption at 565 cm^{-1}. X-ray photoelectron spectroscopy (XPS) showed Si 2p and Cl 2p emissions [Figure 1c,d and Figure S1a in the Supporting Information (SI)], further supporting the chloride surface termination. The UV−vis spectrum of Cl-SiNCs in dichloromethane (Figure S1b) shows a featureless absorption characteristic of SiNCs.[27] The Cl-SiNCs photoluminesce in the blue region of the visible spectrum with an emission maximum at 465 nm (Figure S1b). The origin of this emission is a subject of ongoing investigation.

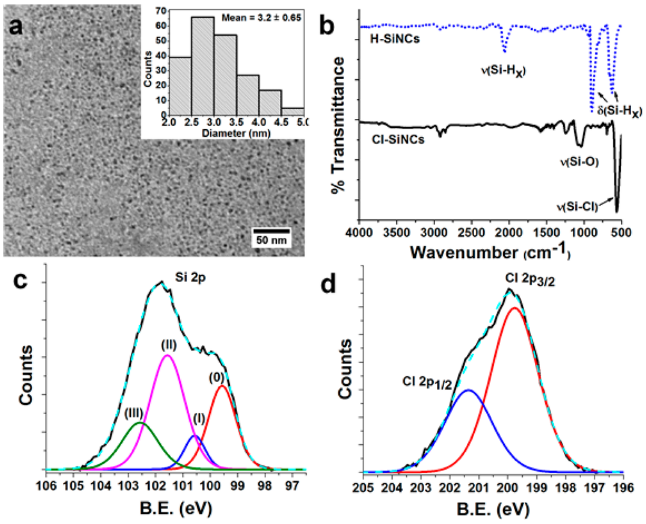


Figure 1. (a) Bright-field TEM image of Cl-SiNCs (inset: particle size distribution). (b) FTIR spectra of H-SiNCs (dotted trace) and Cl-SiNCs (solid trace). (c) Si 2p and (d) Cl 2p regions of the high-resolution XP spectra of Cl-SiNCs.

A modified literature procedure derived from that reported by Senkovskyy et al.[28] was employed to obtain **1** from the Grignard metathesis reaction of 7.5 mmol of 2-bromo-3-hexyl-5-iodothiophene (Br-HT-I) with 8 mmol of *tert*-butylmagnesium chloride in 70 mL of dry tetrahydrofuran (THF). Following preparation, the THF solution of **1** was transferred directly to a Schlenk flask charged with ca. 15 mg of Cl-SiNCs, and the mixture was stirred at room temperature for 6 h under argon followed by quenching upon addition of 20 mL of 5 M aqueous HCl. The crude product mixture was extracted into $CHCl_3$ (ca. 30 mL). The resulting red solution was washed with water (3 × 30 mL), passed through silica gel, and concentrated to dryness under vacuum to yield a red solid. This solid was dissolved in a minimum volume of $CHCl_3$, and a red precipitate was obtained upon addition of excess methanol. The pure solid product (912 mg, 73% yield) was collected by vacuum filtration, dried in vacuo, and evaluated using MALDI-TOF mass spectrometry, ^{1}H NMR spectroscopy, gel-permeation chromatography (GPC), and UV−vis and photoluminescence (PL) spectroscopy.

The formation of P3HT was first evaluated by MALDI-TOF analysis (Figure 2). The spectrum reveals two overlapping patterns with peak separations of m/z 166 corresponding to the molecular weight of the hexylthiophene repeat unit. Mass peaks at m/z 1652.7 and 1574.8 arise from hexylthiophene oligomers consisting of nine repeat units with Br/Br and H/Br end-capping, respectively. High-resolution isotope patterns are provided in Figure S2.

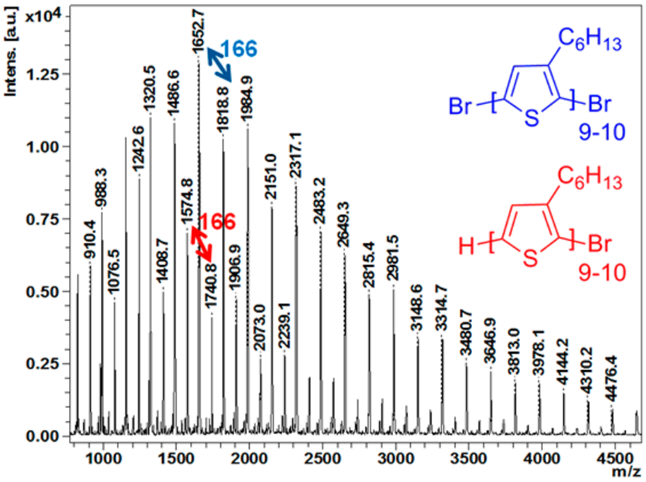


Figure 2. MALDI-TOF mass spectrum of P3HT obtained from a 6 h reaction of **1** in the presence of Cl-SiNCs.

^{1}H NMR analysis (Figure 3) of the product showed broad signals consistent with P3HT. The signal centered at ca. 6.98 ppm is readily attributed to the aromatic proton on the thiophene ring. Consistent with previous assignments, protons on the pendant hexyl groups appear as broadened complex multiplets: α-methylene protons appear at 2.80 and 2.58 ppm; β- and other methylene protons at 1.69, 1.43, 1.34, 1.26 ppm; and terminal methyl group protons at 0.9 ppm.[10] The regioregularity of P3HT can be readily evaluated on the basis of the integration of the α-methylene proton signals (Figure 3, right inset). From this analysis we conclude that the present polymer is a mixture of ca. 68% regioregular head-to-tail (HT) and 32% regiorandom head-to-head (HH) and tail-to-tail (TT) coupling. The expanded ^{1}H NMR spectrum in the aromatic region is also indicative of four different types of couplings (Figure 3, left inset): HT−HT (6.98 ppm), TT−HT (7.00 ppm), HT−HH (7.02 ppm), and TT−HH (7.05 ppm).[10]

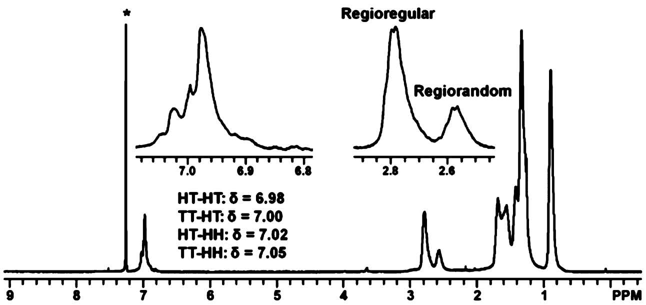


Figure 3. ^{1}H NMR spectra of P3HT in $CDCl_3$ obtained after a 6 h reaction of **1** in the presence of Cl-SiNCs (* indicates a residual solvent peak).

GPC analysis of the P3HT product provided a number-average molecular weight (M_n) of ca. 4k, a weight-average molecular weight (M_w) of ca. 10k, and a polydispersity index (PDI) of ca. 2.5. The polymer molecular weight obtained from this reaction is low relative to those for standard metal-based Lewis acid-mediated P3HT polymerizations (i.e., M_w = 20−40 k), but this is not unexpected given the relatively weak Lewis acidity of Cl-SiNCs. The present PDI is typical for oxidative polymerization methods.[14]

Evaluation of the optical properties of the present P3HT is crucial if these materials are to find future applications in optoelectronic devices.[14,29,30] UV–vis spectroscopy was performed on chloroform solutions of P3HT and thin solid films drop-cast from this solution onto quartz wafers. The solution-phase spectrum (Figure 4a, dotted trace) shows a characteristic broad absorption at λ_{max} = 431 nm; a slight red shift to λ_{max} = 451 nm is noted for the cast films (Figure 4a, solid trace). This red shift has been previously attributed to the increased conjugation resulting from interchain interactions of P3HT in solid films due to π–π stacking.[14,30,31] In addition, the absorption bandwidth is broader for the films, tailing out to ca. 650 nm.

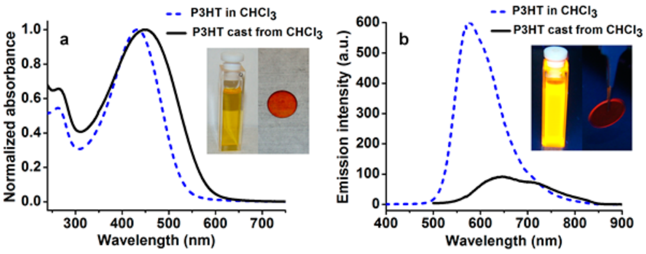


Figure 4. (a) UV–vis absorption spectra and (b) PL emission spectra upon excitation at 350 nm for P3HT obtained from a 6 h reaction with Cl-SiNCs, recorded on a 0.05 mg/mL solution in $CHCl_3$ (dotted trace) and a solid film (solid trace). Insets show the P3HT solution in $CHCl_3$ and the solid film under ambient light and UV excitation, respectively.

Another characteristic P3HT property is its photoluminescence. PL spectra of the present P3HT are shown in Figure 4b. The spectrum obtained from a $CHCl_3$ solution affords a featureless emission with a maximum at 570 nm tailing out to 800 nm (dotted trace). The PL maximum shifts to longer wavelengths for the solid film deposited from $CHCl_3$ solution, showing a peak emission at 647 nm and two shoulder features at 725 and 823 nm (solid trace). The appearance of the low-energy shoulder features has previously been attributed to polaron formation in solid films.[32]

To support our hypothesis that the polymerization reaction arises as a consequence of the Lewis acidity of the Cl-SiNCs and to eliminate possible contributions from monomer photooxidation, we performed identical reactions in the presence and absence of light (Table S1 in the SI). The two reactions afforded equivalent products. Furthermore, an additional control reaction performed under ambient light in the absence of Cl-SiNCs yielded no polymer (Figure S3).

Having established that the reaction of **1** with Cl-SiNCs provides P3HT under the presented conditions, we endeavored to evaluate other Si–Cl-containing species for similar reactivity. In this context, we performed equivalent reactions with Cl-SiWFs [p-type Si(111) wafers; double side polished; 1 × 2 cm^2] and silicon tetrachloride. Qualitative inspection of the color of the reaction mixture suggested negligible polymer formation after 6 h. Extending the reaction time to 24 h afforded a red solution consistent with polymer formation. MALDI-TOF analysis of the isolated products revealed that the reaction catalyzed by Cl-SiWFs afforded H/Br- and Br/Br-terminated P3HT with the number of repeat units ranging from 6 to 22 (Figure S4a). The M_n, M_w, and PDI of the polymer obtained from Cl-SiWFs were 4.0k, 9.5k, and 2.4, respectively. Polymerization of **1** induced by $SiCl_4$ provided P3HT with H/H-terminated P3HT as a major product, as evidenced by MALDI-TOF analysis (Figure S4b). GPC evaluation provided M_n, M_w, and PDI of 3.9k, 8.4k, and 2.1, respectively. Similar to the observations made for polymers prepared using Cl-SiNCs, ^1H NMR analysis (Figure S5) revealed the polymers obtained from the reactions of **1** with Cl-SiWFs and $SiCl_4$ to be 64 and 62% regioregular (HT), respectively. The optical properties of the polymers obtained from these reactions are equivalent to those of the P3HT obtained from Cl-SiNCs (Figure S6).

To obtain a more direct comparison of the catalytic efficiencies of Si–Cl-containing reagents, we performed reactions using each catalyst under identical conditions. The present comparison of catalytic performance cannot be viewed as strictly quantitative because knowing the exact number of catalytic sites for Cl-SiNCs and Cl-SiWFs is impossible. Still, we believe that this comparison provides valuable insight into the origin of our observations. The results are summarized in Table S1. Reactions with all three catalysts produced polymer, and the M_n, M_w, and yield were highest for the product of the reaction involving Cl-SiNCs. These data are consistent with the qualitatively slower reactions noted for the Cl-SiWF and $SiCl_4$ catalysts and indicate that the high surface area and surface Lewis acidity of the Cl-SiNCs play important roles in the observed reactivity.

In conclusion, three silicon-based metal-free catalysts were employed to prepare P3HT. These catalysts have various attractive features, including reasonable reaction times and straightforward separation from the target products. The presented syntheses of the workhorse conjugated polymer P3HT indicate that abundant silicon-based catalysts offer alternative approaches for the preparation of functional materials free from costly and potentially harmful transition metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, polymer characterization, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jveinot@ualberta.ca

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors recognize NSERC for continued generous support. Dr. Eric Rivard and William Torres Delgado are thanked for the assistance with GPC analysis. Thanks are conveyed to all Veinot Team members, including Dr. Muhammad Iqbal, Dr. Mita Dasog, and Leah Coumont for their thoughtful discussions and experimental assistance.

■ REFERENCES

(1) Zhang, Y.; Ziegler, D.; Salmeron, M. *ACS Nano* **2013**, *7*, 8258–8265.

(2) Forrest, S. R. *Nature* **2004**, *428*, 911–918.

(3) Guilbert, A. A. Y.; Reynolds, L. X.; Bruno, A.; MacLachlan, A.; King, S. P.; Faist, M. A.; Pires, E.; Macdonald, J. E.; Stingelin, N.; Haque, S. A.; Nelson, J. *ACS Nano* **2012**, *6*, 3868–3875.

(4) Berggren, M.; Richter-Dahlfors, A. *Adv. Mater.* **2007**, *19*, 3201−3213.
(5) Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459−1463.
(6) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9−12.
(7) Kobayashi, M.; Chen, J.; Chung, T. C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77−86.
(8) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346−1347.
(9) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70−72.
(10) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244.
(11) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817−7823.
(12) Wu, S.; Huang, L.; Tian, H.; Geng, Y.; Wang, F. *Macromolecules* **2011**, *44*, 7558−7567.
(13) Niemi, V. M.; Knuuttila, P.; Osterholm, J. E.; Korvola, J. *Polymer* **1992**, *33*, 1559−1562.
(14) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281−2305.
(15) Jin, S.; Xue, G. *Macromolecules* **1997**, *30*, 5753−5757.
(16) Helgesen, M.; Sondergaard, R.; Krebs, F. C. *J. Mater. Chem.* **2010**, *20*, 36−60.
(17) Liu, R. C.; Liu, Z. P. *Chin. Sci. Bull.* **2009**, *54*, 2028−2032.
(18) Denmark, S. E.; Beutner, G. L.; Wynn, T.; Eastgate, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 3774−3789.
(19) Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428−2429.
(20) Baldwin, R. K.; Pettigrew, K. A.; Ratai, E.; Augustine, M. P.; Kauzlarich, S. M. *Chem. Commun.* **2002**, 1822−1823.
(21) Li, Q.; He, Y.; Chang, J.; Wang, L.; Chen, H.; Tan, Y.; Wang, H.; Shao, Z. *J. Am. Chem. Soc.* **2013**, *135*, 14924−14927.
(22) Dasog, M.; De los Reyes, G. B.; Titova, L. V.; Hegmann, F. A.; Veinot, J. G. C. *ACS Nano* **2014**, *8*, 9636−9648.
(23) Wheeler, L. M.; Neale, N. R.; Chen, T.; Kortshagen, U. R. *Nat. Commun.* **2013**, *4*, No. 2197.
(24) Ashby, E. C.; Bowers, J. R., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 2242−2250.
(25) Yuan, C.; Fang, Q. *RSC Adv.* **2012**, *2*, 8055−8060.
(26) Hessel, C. M.; Henderson, E. J.; Veinot, J. G. C. *Chem. Mater.* **2006**, *18*, 6139−6146.
(27) Wilcoxon, J. P.; Samara, G. A. *Appl. Phys. Lett.* **1999**, *74*, 3164−3166.
(28) Senkovskyy, V.; Tkachov, R.; Beryozkina, T.; Komber, H.; Oertel, U.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 16445−16453.
(29) Mihailetchi, V. D.; Xie, H.; de Boer, B.; Koster, L. J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699−708.
(30) Chang, J.-F.; Sun, B.; Breiby, D. W.; Nielsen, M. M.; Soelling, T. I.; Giles, M.; McCulloch, I.; Sirringhaus, H. *Chem. Mater.* **2004**, *16*, 4772−4776.
(31) He, G.; Kang, L.; Torres Delgado, W.; Shynkaruk, O.; Ferguson, M. J.; McDonald, R.; Rivard, E. *J. Am. Chem. Soc.* **2013**, *135*, 5360−5363.
(32) Cook, S.; Furube, A.; Katoh, R. *Energy Environ. Sci.* **2008**, *1*, 294−299.