

(Supporting Information)

**Template-Synthesized Nanostructure Morphology Influenced by Molecular
Building Blocks**

David Huesmann, Paul M. DiCarmine, and Dwight S. Seferos*

Department of Chemistry, Lash Miller Chemical Laboratories, University of Toronto,
Toronto, Ontario, M5S 3H6, Canada

Department of Chemistry, Johannes-Gutenberg Universität, Duesbergweg 10-14, 55099
Mainz, Germany

Email: dseferos@chem.utoronto.ca

Table of Contents

Monomer Synthesis	S3
Preparation of Surface-Anchored Nanostructures	S6
Preparation of Template-Cross Sections	S6
Behavior of thiophene and 3-hexylthiophene nanostructures in different solvents	S6
Additional References	S7

List of Reaction Schemes

Scheme S1 Synthetic route used to prepare 3-(2-ethyl)hexylthiophene	S3
Scheme S2 Synthetic route used to prepare 3-(2-(2-(2-ethoxy)ethoxy)ethoxy)methylthiophene	S4

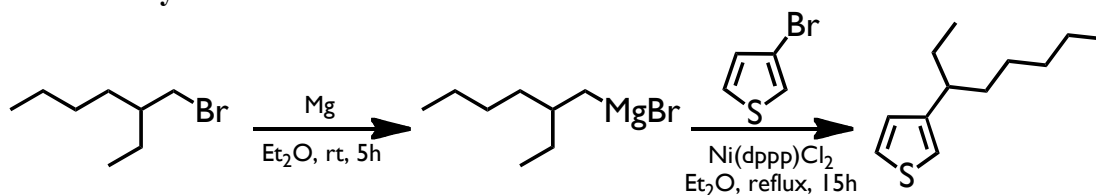
List of Figures

Fig. S 1 TEM images of thiophene nanostructures grown for 20, 40, and 100 minutes	8
Fig. S 2 SEM image of thiophene nanostructure cross-section	9
Fig. S 3 Representative TEM and SEM images of thiophene, 3-hexylthiophene, and 3-(2-ethyl)hexylthiophene nanostructures	10
Fig. S 4 Representative TEM images of 3-(2-ethyl)hexylthiophene and 3-(hydroxy)methylthiophene nanostructures	11
Fig. S 5 Photograph of a centrifuge tube of isolated thiophene and 3-hexylthiophene nanostructures in water	12
Fig. S 6 X-ray diffraction data for thiophene and 3-hexylthiophene nanostructures	13
Fig. S 7 EDX map of thiophene nanostructures	14
Fig. S 8 EDX map of 3-hexylthiophene nanostructures	15
Fig. S 9 Absorbance spectra of thiophene, selenophene, and thieno[3,2- <i>b</i>]thiophene in acetonitrile.....	16

List of Tables

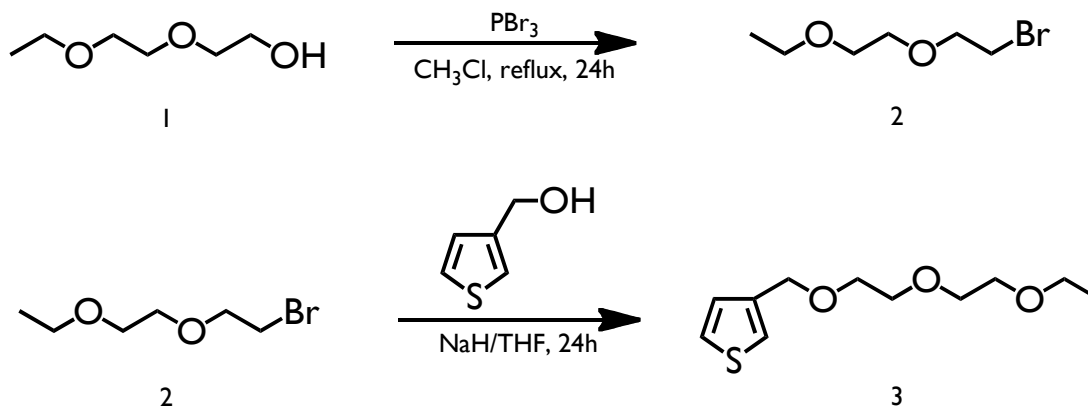
Table S1 Behavior of thiophene and 3-hexylthiophene nanostructures in different solvents	S6
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Monomer Synthesis



Scheme S1 Synthetic route used to prepare 3-(2-ethyl)hexylthiophene.

3-(2-Ethyl)hexylthiophene. This reagent was prepared according to literature procedures (Scheme S1).¹ Briefly, magnesium (177 mg, 7.28 mmol) was suspended in 3 mL of diethyl ether under a nitrogen atmosphere in a dried 25 mL three-neck round-bottom flask containing a magnetic stir bar and fitted with a condenser. 2-(Ethyl)hexylbromide (1.28 mL, 7.16 mmol) in 3 mL of diethyl ether was then added dropwise to the magnesium suspension via syringe. An exothermic reaction began after 5 minutes and the mixture was stirred until nearly all magnesium had dissolved (5 h). The soluble components were then transferred into another round-bottom flask (containing a magnetic stir bar and fitted with a condenser) via syringe. 3-Bromothiophene (0.61 mL, 6.4 mmol) and Ni(1,3-bis(diphenylphosphino)propane)Cl₂ (15 mg, 0.028 mmol) were added and the solution was refluxed for 15 h and then quenched with ice and 2 M HCl. The aqueous phase was extracted 3 times with diethyl ether and the organic layer was concentrated by rotary evaporation to yield an orange liquid. The crude product was purified by column chromatography in hexanes:dichloromethane (25:1) to afford a colorless liquid which was further purified by vacuum distillation to yield 755 mg (3.85 mmol, 60%) of the title compound. ¹H NMR (400 MHz, CDCl₃) δ = 7.23 (dd, J = 4.9, 3.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 2.57 (d, J = 6.9 Hz, 2H), 1.61 – 1.50 (m, 1H), 1.33 – 1.19 (m, 8H), 0.96 – 0.79 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ = 142.01, 128.90, 124.92, 120.78, 40.57, 34.45, 32.69, 29.08, 25.80, 23.21, 14.28, 11.00. MS-EI: 196.1288 Δ = 1 ppm.



Scheme S2 Synthetic route used to prepare 3-(2-(2-(2-ethoxyethoxy)methylthiophen-3-yl)ethoxy)ethoxyethane.

1-Bromo-2-(2-ethoxyethoxyethane (2). 2-(2-Ethoxyethoxyethanol (1) (10.0 mL, 73.6 mmol) was dissolved in 20 mL of chloroform under a nitrogen atmosphere in a dried 50 mL three-neck round-bottom flask containing a magnetic stir bar and fitted with a condenser. The flask was immersed in an ice bath and phosphorous tribromide (PBr_3 , 7.0 mL, 73.6 mmol) was added at which time an exothermic reaction began. Once the exothermic reaction subsided, the mixture was heated and allowed to reflux overnight. The mixture was then cooled to room temperature, poured into ice, and neutralized with 1 M NaOH (150 mL). The organic phase was washed 3 times with water and concentrated by rotary evaporation. The product was purified by vacuum distillation (28.5 mm Hg). The fraction collected between 47–53°C contained 8.99 g (45.8 mmol, 62%) of the title compound (2), a colorless, strongly scented liquid. ^1H NMR (300 MHz, CDCl_3) δ = 3.82 (t, J = 6.4 Hz, 2H), 3.70 – 3.44 (m, 8H), 1.22 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ = 71.45, 70.82, 70.01, 66.93, 30.43, 15.36. MS-ESI: 197.0171 Δ = 2.7 ppm.

3-(2-(2-(2-Ethoxy)ethoxy)ethoxy)methylthiophene (3). This reagent was prepared according to literature procedures (Scheme S2).² Briefly, 3-(hydroxy)methylthiophene (0.83 mL, 8.8 mmol) and **2** (1.76 g, 8.95 mmol) were dissolved in 25 mL of tetrahydrofuran under a nitrogen atmosphere in a dried 100 mL Schlenk flask containing a magnetic stir bar. The flask was immersed in an ice bath and sodium hydride powder (NaH, 267 mg, 10.5 mmol) was added while stirring. The reaction was allowed to warm to room temperature and was then left overnight. Water was added and the mixture was filtered through Celite (acid washed standard super-cel NF). The organic phase was separated and concentrated by rotary evaporation. The product was purified by vacuum distillation (28.5 mmHg). The fraction collected between 150–160°C contained the desired product which was further purified by column chromatography in hexanes:ethyl acetate (85:15) to afford 1.05 g (4.55 mmol, 26%) of the pure title compound (**3**), a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ = 7.22 (dd, J = 4.9, 3.0 Hz, 1H), 7.15 (d, J = 2.2 Hz, 1H), 7.01 (dd, J = 4.9, 1.0 Hz, 1H), 3.65 – 3.42 (m, 12H), 1.14 (t, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 139.50, 127.39, 125.91, 122.85, 70.74, 70.69, 69.87, 69.35, 68.48, 66.66, 15.18. MS-EI: 230.0979 Δ = 0.9 ppm.

Preparation of Surface-Anchored Nanostructures

To prepare an array of surface-anchored nanostructures, the template was treated with 3 M NaOH solution in a Petri dish for 1 hour and then washed with water.

Preparation of Template Cross-Sections

Cross sections of AAO templates were prepared after electropolymerization. The electrochemical cell was rinsed two times with diethyl ether and the template was cleaved using two tweezers to achieve a smooth breakline.

Behavior of thiophene and 3-hexylthiophene nanostructures in different solvents

Nanostructures were suspended in a minimal amount of ethanol (10 μ l) and then added to 5 mL of the corresponding solvent. The mixtures were shaken for 24 hours in a small glass vial at 500 rpm. Behavior was determined by visually inspecting the solutions for homogeneous coloration as well as performing TEM analysis to determine whether the nanostructures were still present. The results are summarized in Table S1.

Table S1 Behavior of thiophene and 3-hexylthiophene nanostructures in different solvents.

Solvent	Thiophene Nanostructure	3-Hexylthiophene Nanostructure
Ethanol	suspension	aggregation ^a
DMF	weak aggregation	dispersed
THF	weak aggregation	dispersed
DCM	weak aggregation	dispersed
Et ₂ O	intermediate aggregation	partially dispersed
Toluene	intermediate aggregation	partially dispersed
Hexane	strong aggregation	aggregation

^a started to disperse after 1 month

Additional References

1. C. Van Pham, H. B. Mark Jr. and H. Zimmer, *Synth. Commun.*, 1986, **16**, 689-696.
2. T. Ikeda, M. Higuchi and D. G. Kurth, *J. Am. Chem. Soc.*, 2009, **131**, 9158-9159.

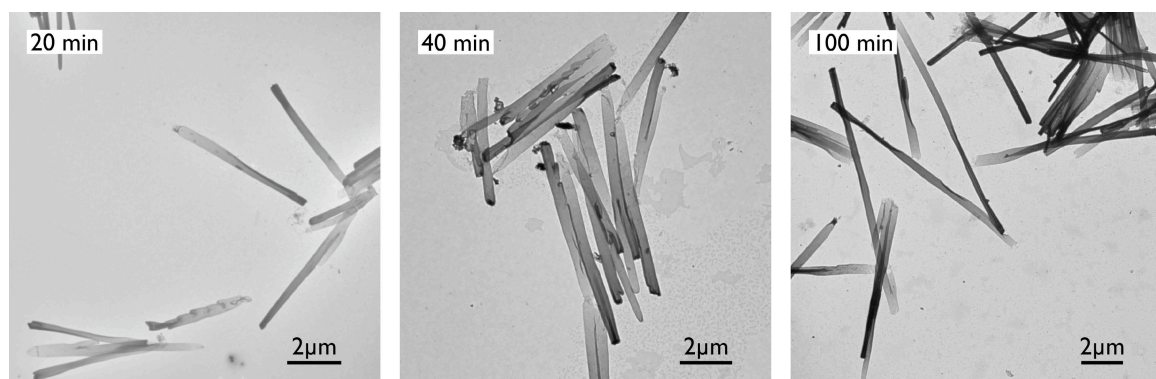


Fig. S 1 TEM images of thiophene nanostructures grown for 20, 40, and 100 minutes.

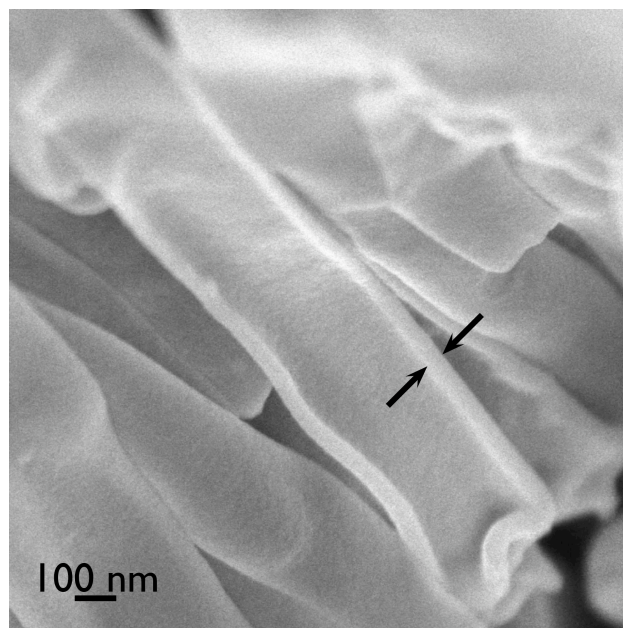


Fig. S 2 SEM image of thiophene nanostructure cross-section. Arrows indicate the side-wall thickness near the base (the end that was previously in contact with the sacrificial metal layer) of the nanostructure (~ 45 nm).

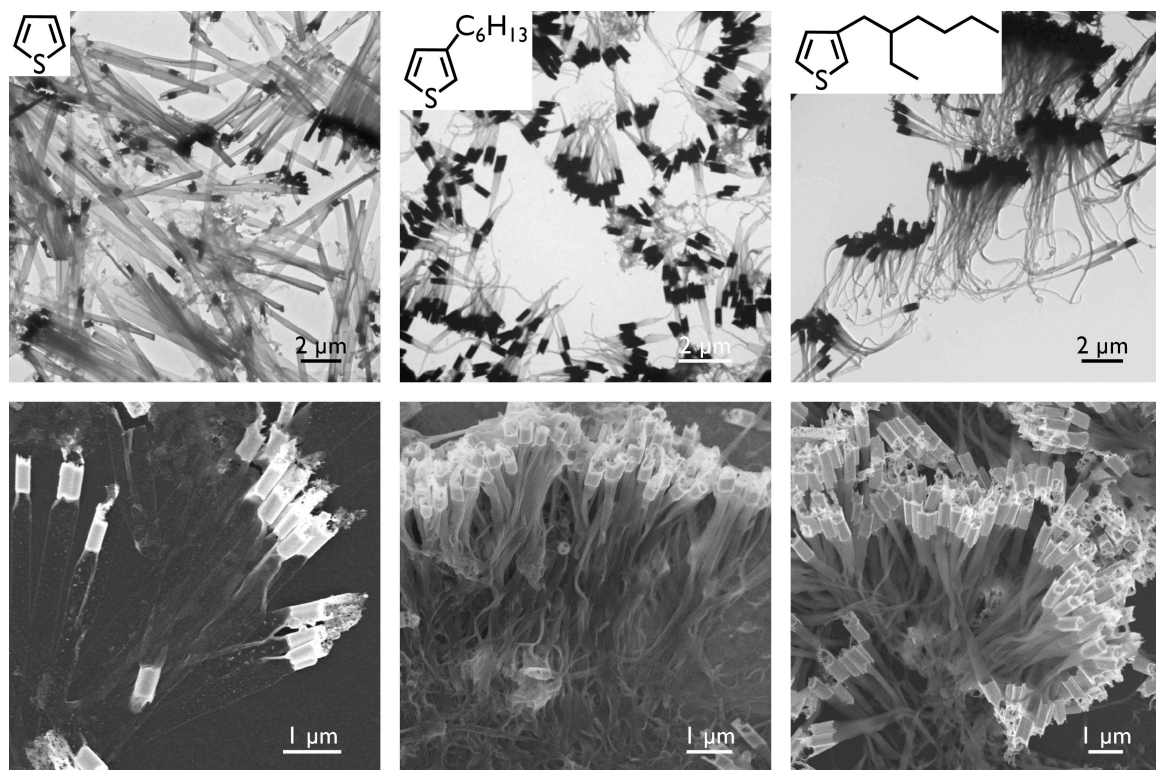


Fig. S 3 Representative TEM (top) and SEM (bottom) images of thiophene (left), 3-hexylthiophene (middle), and 3-(2-ethyl)hexylthiophene (right) nanostructures. Building block structures are inset within the corresponding column. The gold segments were not etched.

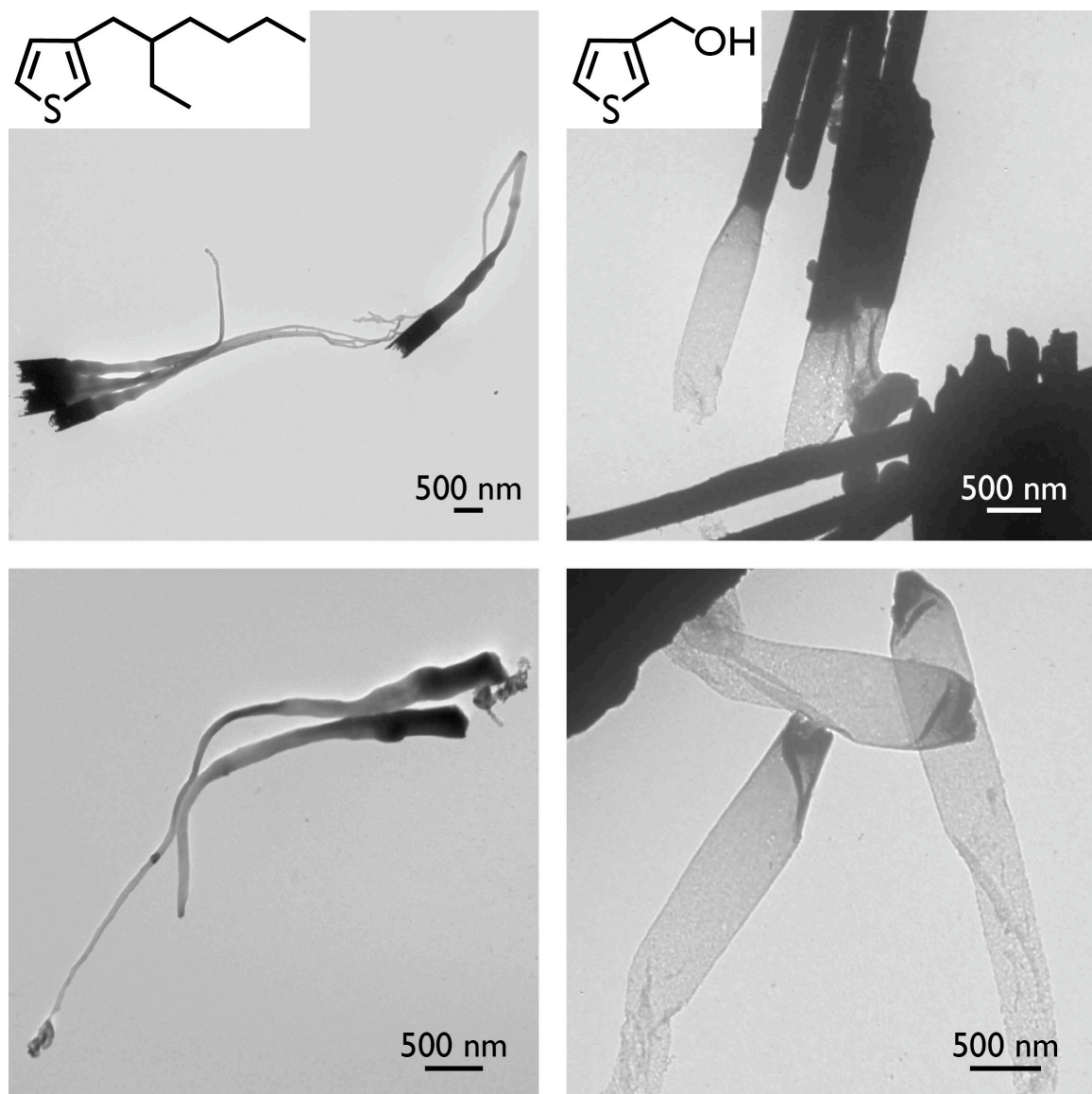


Fig. S 4 Representative TEM images of 3-(2-ethyl)hexylthiophene (left) and 3-(hydroxy)methylthiophene (right) nanostructures. Building block structures are inset within the corresponding column. In the top images the gold segments were not etched. The bottom images were taken after gold etching.

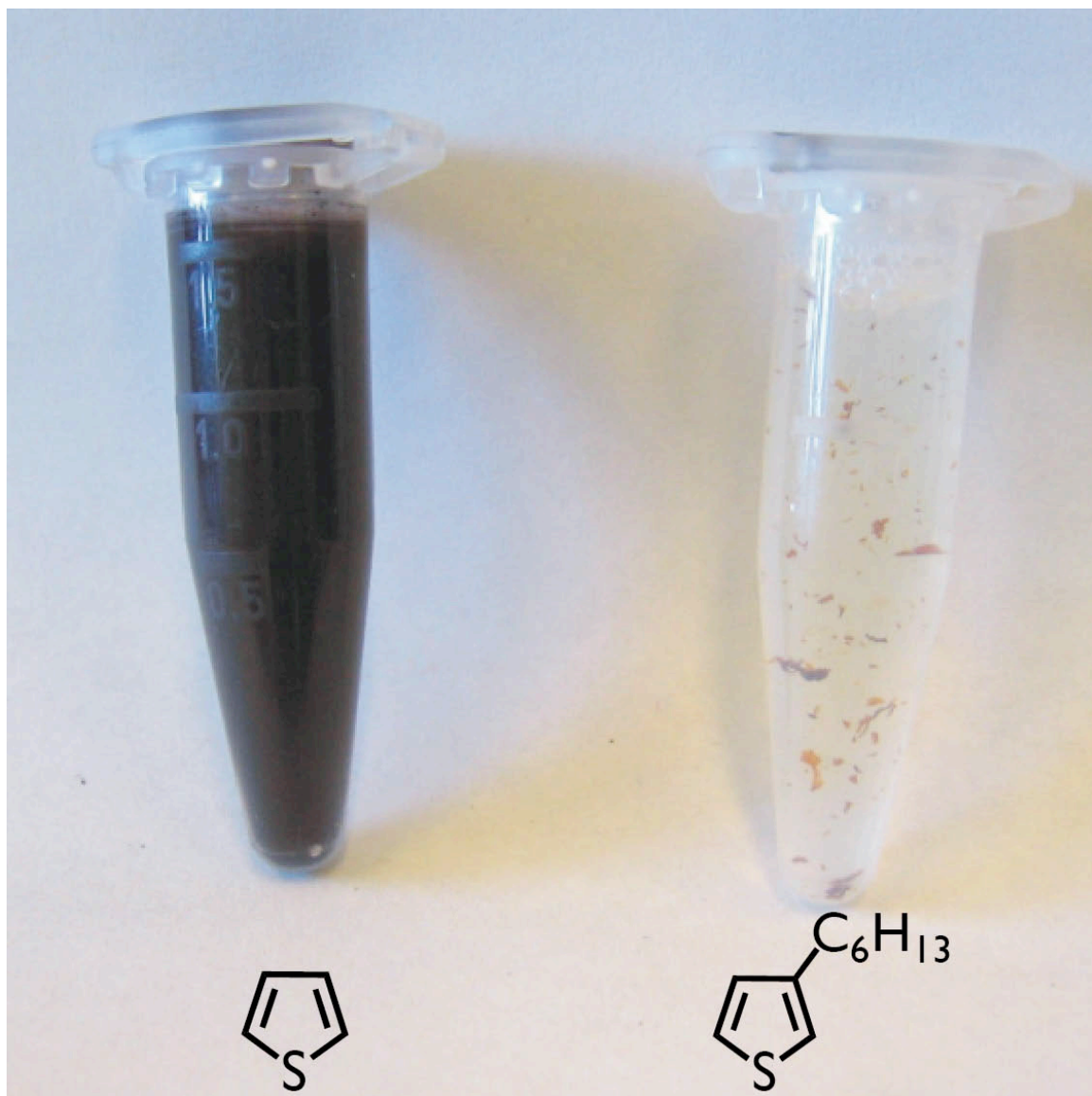


Fig. S 5 Photograph of a centrifuge tube of isolated thiophene (left) and 3-hexylthiophene (right) nanostructures in water. Building block structures are given below the corresponding centrifuge tube.

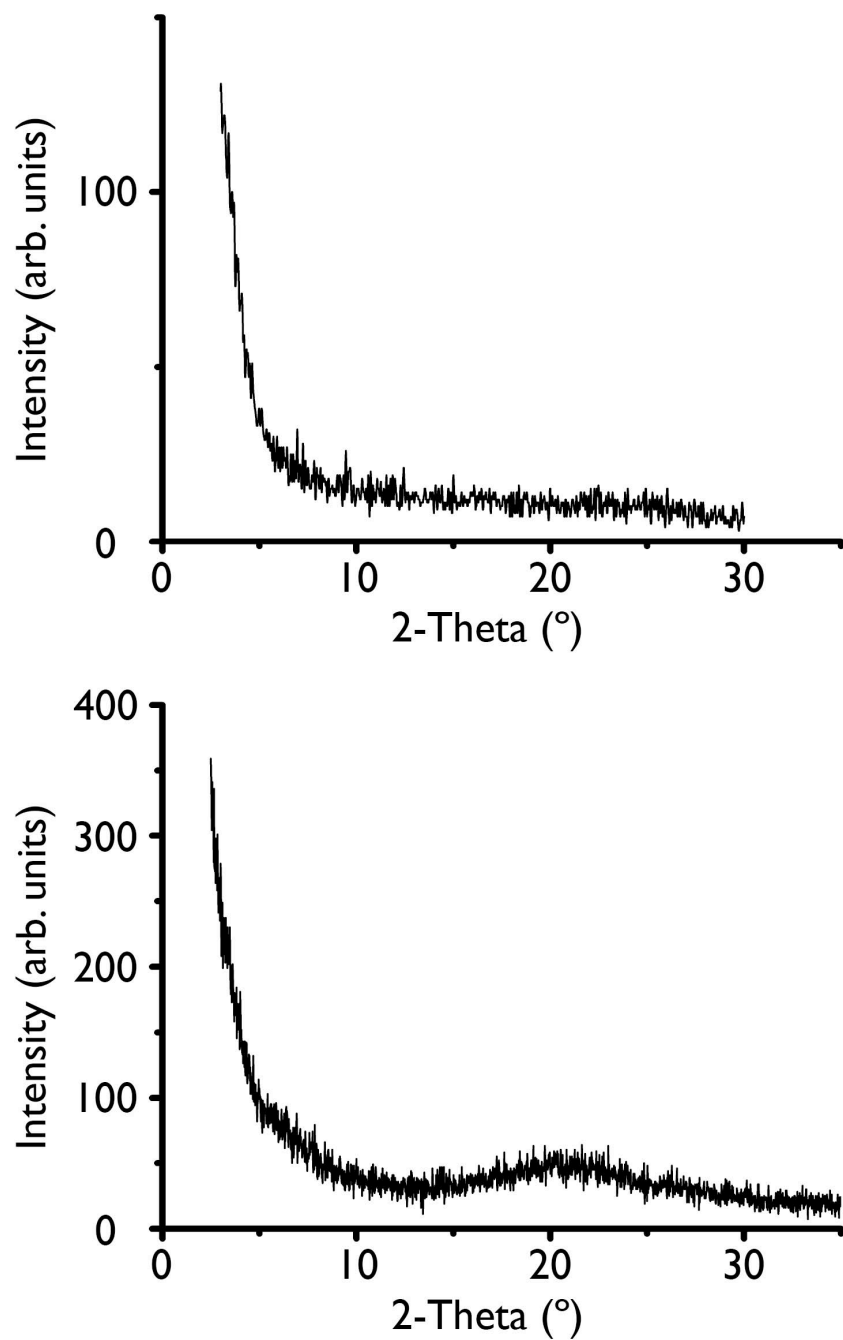


Fig. S 6 X-ray diffraction data for thiophene (top) and 3-hexylthiophene (bottom) nanostructures.

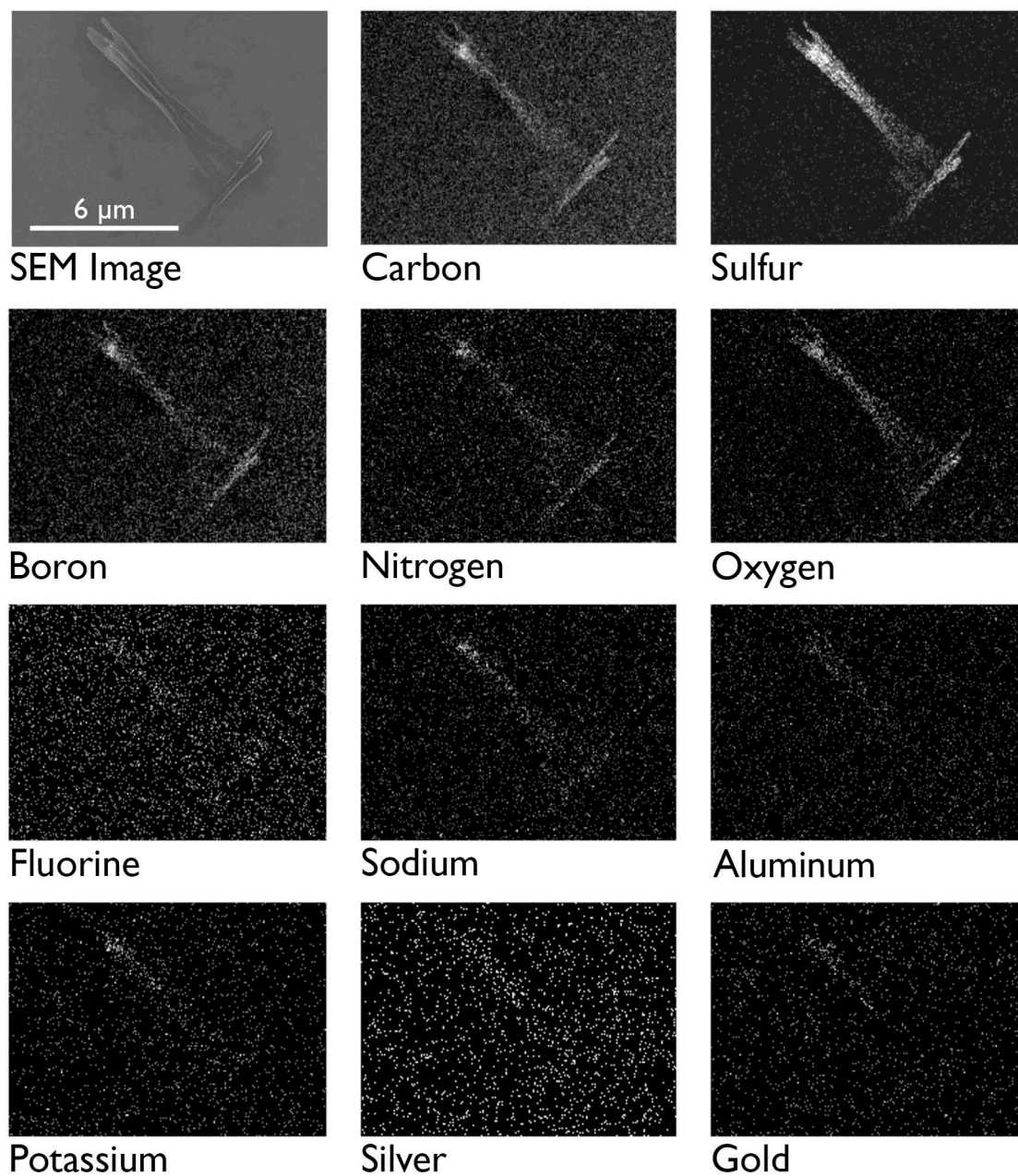


Fig. S 7 Thiophene nanostructures, top left to bottom right: SEM image; and EDX map for Carbon, Sulfur, Boron, Nitrogen, Oxygen, Fluorine, Sodium, Aluminum, Potassium, Silver, and Gold.

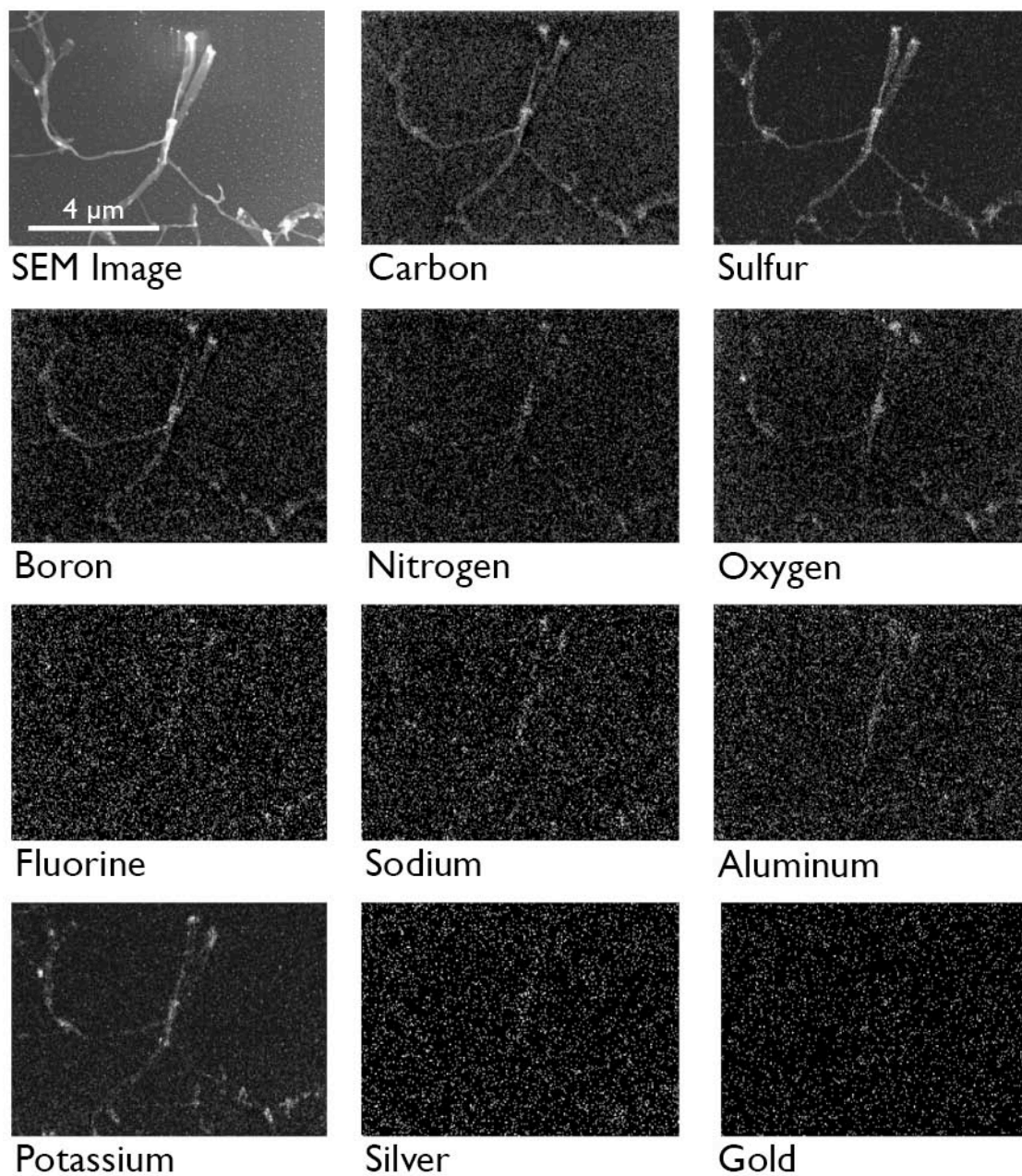


Fig. S 8 3-Hexylthiophene nanostructures, top left to bottom right: SEM image; and EDX map for Carbon, Sulfur, Boron, Nitrogen, Oxygen, Fluorine, Sodium, Aluminum, Potassium, Silver, and Gold.

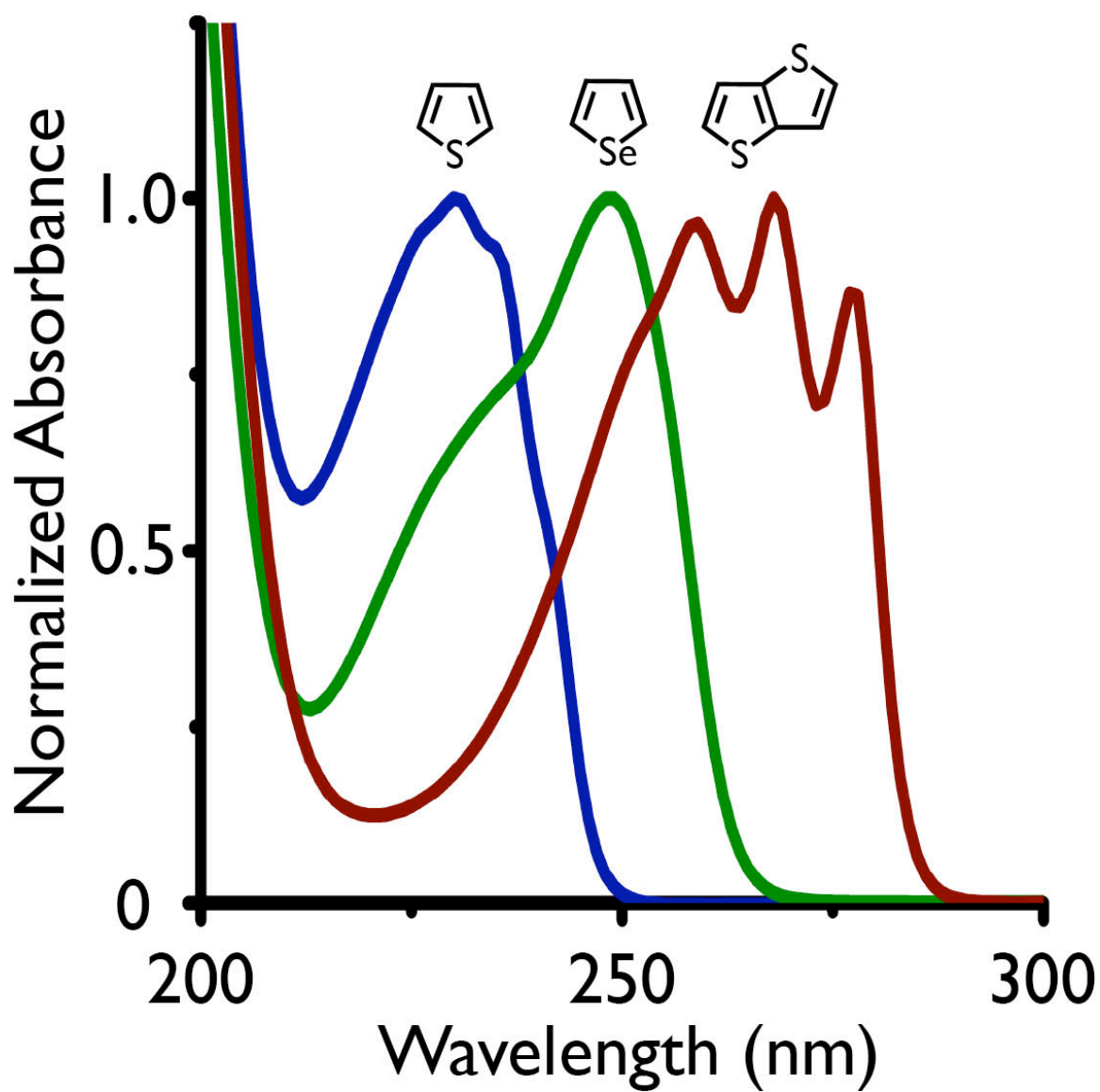


Fig. S 9 Normalized absorbance spectra of thiophene, selenophene, and thieno[3,2-*b*]thiophene in acetonitrile.