

Formation and Analysis of Self-Assembled Monolayers from U-Shaped Oligo(phenylene ethynylene)s as Candidates for Molecular Electronics

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We present the synthesis of novel oligo(phenylene ethynylene)-[1,1';3'1'']terphenyls and oligo(phenylene ethynylene)-1,8-anthracenes and their analyses at the metal–molecule interface when forming self-assembled monolayers (SAMs) on gold surfaces. The target compounds were synthesized with thioacetate functionalities that serve as molecular “alligator clips” upon thiol deprotection, to promote metallic adhesion. The resulting monolayers were studied, and the integrity of the molecule–gold attachment was corroborated by single-wavelength ellipsometry (SWE), cyclic voltammetry (CV), and X-ray photoelectron spectroscopy (XPS). Additionally, the kinetics of SAM formation on a gold electrode were probed by CV, while a clear signal corresponding to the thiol–gold bond was detected by XPS. These conformationally restricted oligomers are designed to be of use in studies utilizing scanning probe microscopy techniques to elucidate switching mechanisms and negative differential resistance behavior thought to be based on molecular conformational changes.

1. Introduction

The rational design and synthesis of molecular candidates for inclusion in the fabrication of molecular-scale devices to be used in electronics and sensing is a focus of our research.¹ In our experience it is best to start with a related series of candidate compounds and to verify their surface assembly characteristics before incorporating them into device test structures. When evaluating an organic molecule for potential application as a molecular device component, the electronic nature of its functional groups as well as its molecular geometry determine, to a great extent, the electronic characteristics.² Recent work has shown experimentally^{3–5} and theoretically^{6,7} that the metal–molecule interface in particular plays a crucial role in the overall conductivity and in some cases the behavior of the whole system.⁸

Several theoretical models have aided in understanding this observed switching behavior. Specifically, changes in electronic conduction of the molecules have been attributed to a wide variety of mechanisms, including reversible reduction⁹ and rotation of functional groups¹⁰ as well as conformationally induced tunnel barriers.¹¹ Several oligo(phenylene ethynylene)s (OPE)s have been identified as possessing favorable characteristics for nonlinear electronic responses,^{12,13} having a low HOMO–LUMO gap relative to the gap in aliphatic chains, and thereby providing electron delocalization along the length of the molecule.¹⁴ Moreover, by lowering the barrier for electron transport when covalently attached to metal surfaces, fully conjugated OPEs can have improved electrical transport.^{15,16} An extended

(1) Tour, J. M. *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming*, World Scientific: River Edge, NJ, 2003.

(2) Mantooh, B. A.; Weiss, P. S. *Proc. IEEE* **2003**, *91*, 1785.

(3) Zhu, X. Y.; Vondrak, T.; Wang, H.; Gahl, C.; Ishioka, K.; Wolf, M. *Surf. Sci.* **2000**, *451*, 244.

(4) Beebe, J. M.; Engelkes, V. B.; Miller, L. L.; Frisbie, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 11268.

(5) Chen, J.; Wang, W.; Klemic, J.; Reed, M. A.; Axelrod, B. W.; Kaschak, D. M.; Rawlett, A. M.; Price, D. W.; Dirk, S. M.; Tour, J. M.; Grubisha, S. D.; Bennett, D. W. In *Molecular Electronics II*; Ann. New York Academy of Science: 2002; Vol. 960, p 69.

(6) Xue, Y. Q.; Datta, S.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 4292.

(7) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*, 086802.

(8) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384.

(9) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.

(10) di Ventra, M.; Pantelides, S. T.; Lang, N. D. *Phys. Rev. Lett.* **2000**, *84*, 979.

(11) Karzazi, Y.; Cornil, J.; Bredas, J. L. *Nanotechnology* **2003**, *14*, 165.

(12) Fan, F. R.; Yang, J.; Cai, L.; Price, D. W.; Dirk, S. M.; Kosynkin, D. V.; Yao, Y.; Rawlett, A. M.; Tour, J. M.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 5550.

(13) Flatt, A. K.; Dirk, S. M.; Henderson, J. C.; Shen, D. E.; Su, J.; Reed, M. A.; Tour, J. M. *Tetrahedron* **2003**, *59*, 8555.

(14) Seminario, J. M.; de la Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616.

(15) Fischer, C. M.; Burghard, M.; Roth, S. *Mater. Sci. Forum* **1995**, *191*, 149.

(16) Lang, N. D.; Avouris, P. P. *Phys. Rev. B* **2001**, *64*, 5323.

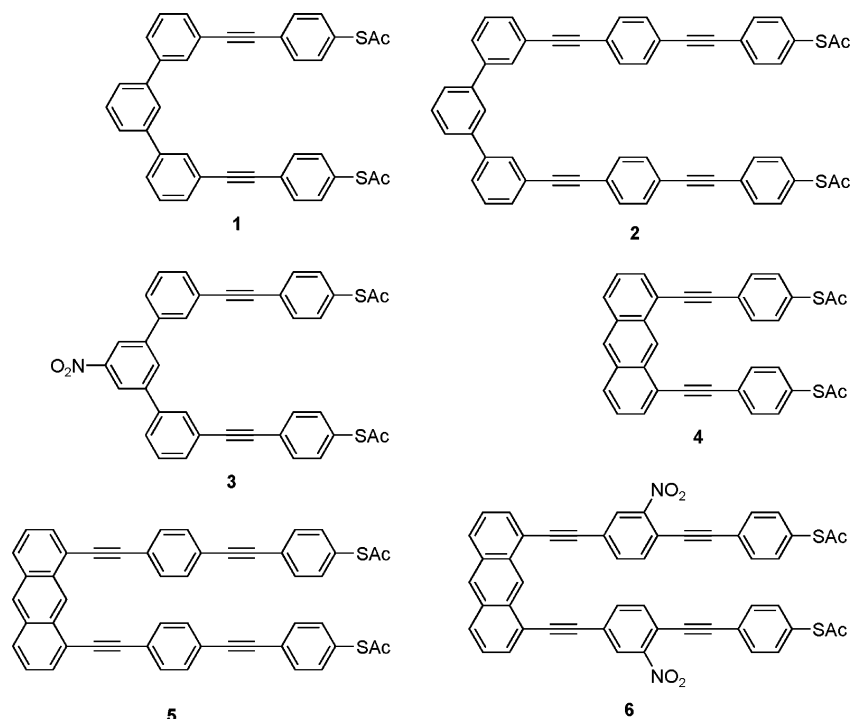


Figure 1. Target compounds 1–6.

π -conjugation throughout the backbone of the molecule is also thought to improve the overlap and delocalization of electron orbitals.¹⁷ With variation in the functional groups and structural rigidity of OPEs, members of this class of compounds have been shown to possess the physical properties necessary to act as high-conductivity wires,^{18–21} rectifiers,²² components showing negative differential resistance (NDR),^{23–26} memory elements,²⁷ and bistable latches,^{28,29} depending on the testbed used.

This has motivated us to pursue the synthesis of new OPEs that have an extended conjugation exemplified by a 1,3-bridging aromatic ring linking two linear phenylethynyl backbones. Six new “U-shaped” OPEs have been synthesized, as shown in Figure 1, based on 3,3'-diethynyl-[1,1';3',1'']terphenyl and 1,8-diethynylanthracene.

We propose that the use of U-shaped molecules will aid in developing a better physical understanding of the electronic properties of OPEs when they are present in

active molecular electronic devices. Oligomers **3** and **6** bear nitro groups as potential redox centers, and all targets are end-functionalized with acetyl-protected molecular alligator clips which upon deprotection afford the thiolates or thiols for covalent surface attachment. The terphenyl targets have a relatively low rotational barrier and larger dihedral angles at the central terphenyl ring, whereas the anthracene derivatives have higher rigidity based on the fully conjugated and planar 1,8-diethynylanthracene backbone.

2. Synthesis

The synthesis of the terphenyl targets began with commercially available 1,3-dibromobenzene, as shown in Scheme 1. A double lithium-bromide exchange reaction and stannylation afforded **7**, which was used with 3-iodoaniline in a Stille coupling reaction³⁰ to provide the terphenyl backbone **8**.

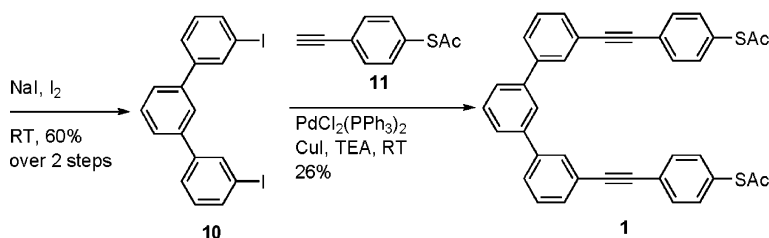
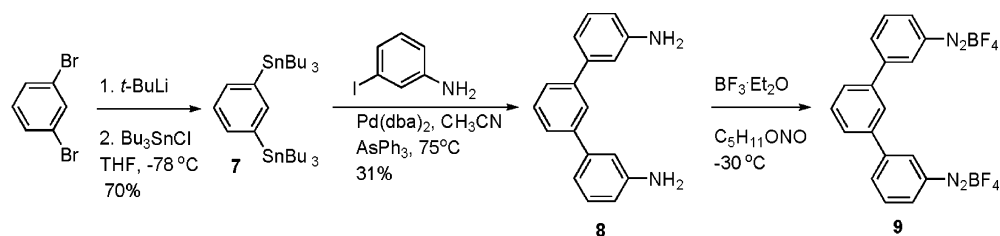
The anilines were then diazotized with isoamyl nitrite and boron trifluoride etherate³¹ to obtain **9**, followed by iodination with sodium iodide and iodine to afford **10**. A final Sonogashira coupling³² with the free alkyne **11** gave the terphenyl **1** as the desired target.

Intermediate **10** was also utilized for the synthesis of a longer terphenyl U-shaped oligomer, as depicted in Scheme 2. 4-Ethynylaniline³³ (**12**) was used in a Sonogashira coupling to afford the bis-aniline **13**. Diazotization and iodination conditions similar to those as in Scheme 1 were followed in order to isolate the

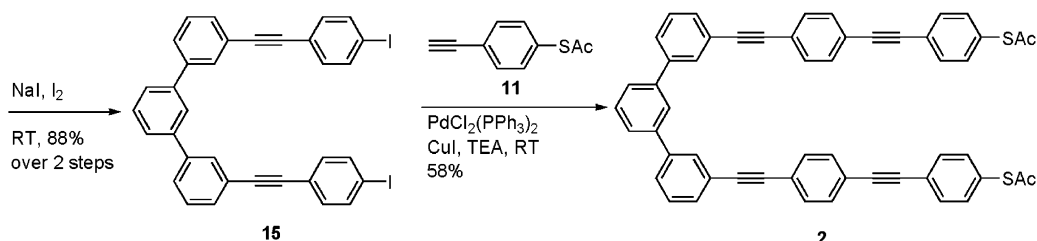
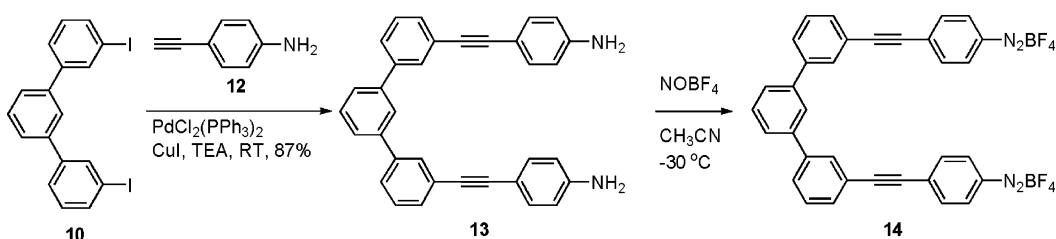
- (17) Magoga M.; Joachim, C. *Phys. Rev. B* **1997**, *56*, 4722.
 (18) Donhauser, Z. J.; Mantooh, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. J.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M. *Science* **2001**, *292*, 2303.
 (19) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
 (20) Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L.; Tour, J. M. *Appl. Phys. Lett.* **1997**, *71*, 611.
 (21) Wassel, R. A.; Fuierer, R. R.; Kim, N.; Gorman, C. B. *Nano Lett.* **2003**, *3*, 1617.
 (22) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224.
 (23) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Science* **1999**, *286*, 1550.
 (24) Amlani, I.; Rawlett, A. M.; Nagahara, L. A.; Tsui, R. K. *Appl. Phys. Lett.* **2002**, *80*, 2761.
 (25) Li, C.; Zhang, D.; Liu, X.; Han, S.; Tang, T.; Zhou, C.; Fan, W.; Koehne, J.; Han, J.; Meyyappan, M.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2003**, *82*, 645.
 (26) Rawlett, A. M.; Hopson, T. J.; Nagahara, L. A.; Tsui, R. K. *Appl. Phys. Lett.* **2002**, *81*, 3043.
 (27) Tour, J. M.; Cheng, L.; Nackashi, D. P.; Yao, Y.; Flatt, A. K.; St. Angelo, S. K.; Mallouk, T. E.; Franzone, P. D. *J. Am. Chem. Soc.* **2003**, *125*, 13279.

- (28) Chen, Y.; Ohlberg, D. A.; Li, X.; Stewart, D. R.; Williams, R. S.; Keppens, J. O.; Nielsen, K. A.; Stoddart, J. F.; Olynick, D. L.; Anderson, E. *Appl. Phys. Lett.* **2003**, *82*, 1610.
 (29) Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2001**, *78*, 3735.
 (30) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
 (31) Kosynkin, D. V.; Tour, J. M. *Org. Lett.* **2001**, *3*, 991.
 (32) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.
 (33) Dirk, S. M.; Price, D. W.; Chanteau, S. H.; Kosynkin, D. V.; Tour, J. M. *Tetrahedron* **2001**, *57*, 5109.

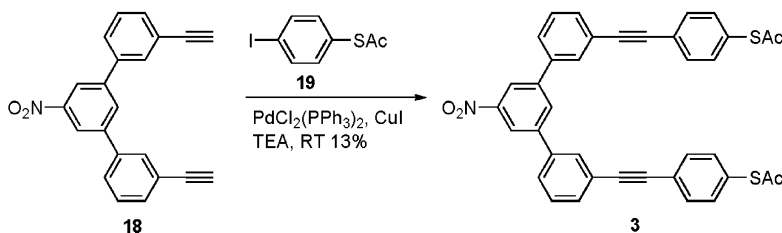
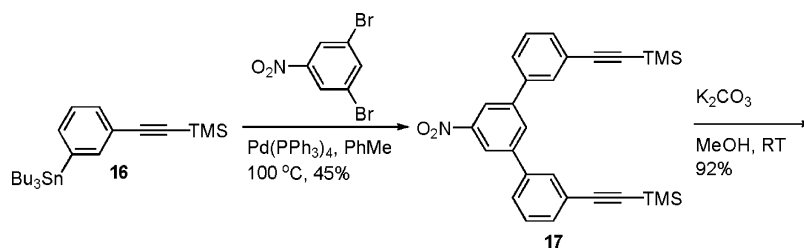
Scheme 1



Scheme 2



Scheme 3



terphenyl **15**. A final coupling with the free alkyne **11** provided the final target **2** in moderate yield.

The third terphenyl U-shaped target **3** was prepared with a nitro group at the apex position as depicted in Scheme 3, starting with **16** which was prepared in 63% yield over two steps from 1,3-dibromobenzene.³⁴

A Stille coupling between **16** and 1,3-dibromo-5-nitrobenzene afforded **17**. Alkaline deprotection of the

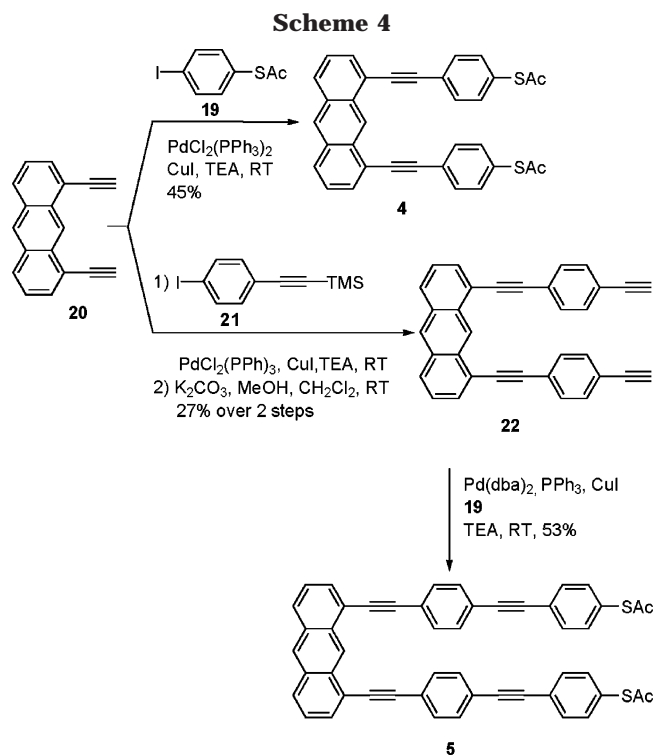
alkynes gave **18**, which was then coupled with alligator clip **19**³⁵ to afford the desired oligomer **3**.

The synthesis of the anthracene-based U-shaped molecules started with 1,8-diethynylantracene **20**³⁶ as

(34) Price, D. W.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497.

(35) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.

(36) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179.



depicted in Scheme 4. Sonogashira coupling with alligator clip **19** afforded the anthracene oligomer **4**.

Conveniently, the same starting material, **20**, and similar synthetic steps were used for the construction of a longer U-shaped target, also shown in Scheme 4. Compound **20** was coupled with iodide **21** followed by deprotection of the alkyne affording **22**. Subsequent coupling with alligator clip **19** yielded the target oligomer **5**.

As illustrated in Scheme 5, a similar anthracene-based U-shaped molecule containing two nitro functional groups was also synthesized.

4-Bromo-3-nitroaniline³⁷ was coupled with TMSA to afford **23**. The aniline was then diazotized and converted to the aryl iodide following known conditions³¹ to afford **24**. Sonogashira coupling with 1,8-diethynylantracene (**20**) gave the bis-TMS-protected alkyne **25**. A final alkaline deprotection followed by coupling with alligator clip **19** gave the desired dinitro oligomer **6**.

3. Assembly

The thioacetyl groups of these compounds could be easily removed to the free thiol or thiolate by deacylation with NH_4OH , as described previously.³⁸ Subsequent exposure to a gold surface results in the formation of a Au–S bond. Unlike the assembly of oligomers containing one alligator clip,³⁹ the U-shaped OPEs reported here feature two thiolates capable of forming Au–S bonds to the surface. While the planarity enforced by the anthracene backbone of OPEs **4–6** increased the probability that both thiols would participate in the

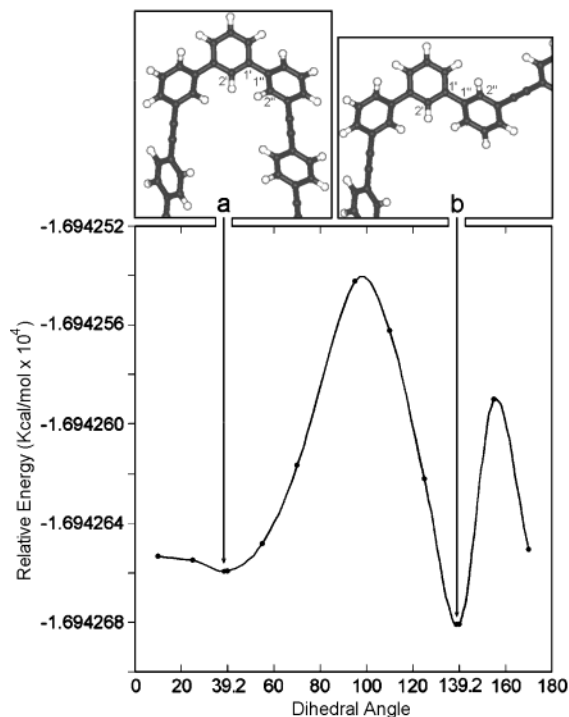


Figure 2. Calculated energies for oligomer **2**. The dihedral angle values correspond to $\text{C}_2\text{-C}_1\text{-C}_1'\text{-C}_2'$ of the terphenyl moiety. The lowest calculated energies were observed at 39° (structure a) and 139° (zigzag structure b).

SAM formation, the terphenyl backbone of OPEs **1–3** has more rotational freedom that could result in incomplete SAM formation and higher defects in surface coverage.

Our calculations corroborated this conjecture. Figure 2 shows calculated energies for oligomer **2** at different dihedral angles of the terphenyl moiety.⁴⁰

Two local minima were found, corresponding to dihedral angles of 39° and 139° . The range between the highest and the lowest energy (going from dihedral angle of 95° to 139° , Figure 2) is only 0.14 Kcal, indicating the free rotation of the terphenyl backbone. It is at the dihedral angle of 139° that the two alligator clips are at opposite ends of a zigzag structure, and it is this conformation that may lead to SAMs with defects and a less ordered organic monolayer. To better understand these calculations, experimental analysis at the interface level was performed using cyclic voltammetry (CV), single wavelength ellipsometry (SWE), and X-ray photoelectron spectroscopy (XPS).

4. Monolayer Analysis

Monolayer formation on a gold electrode was monitored by CV. Ion currents at the electrode under applied bias are an indirect measure of defect densities in the SAM. Figure 3 shows the results of CV tests done at increasing times for SAMs formed, using compound **4** on a working Au electrode by applying a potential in aqueous solutions with 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl.

After 15 min of assembly, CV showed that the redox current was decreased by slightly more than half, and

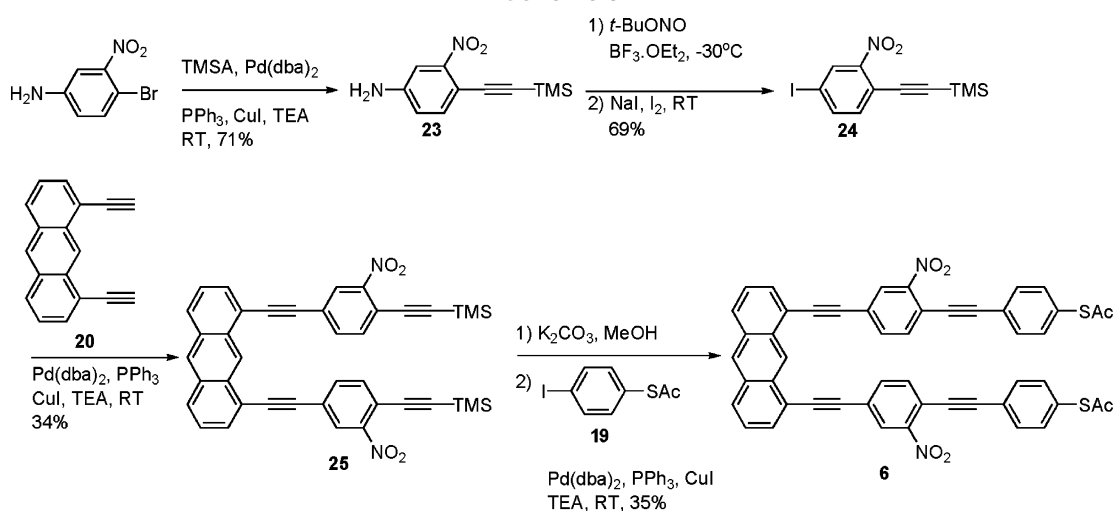
(37) Sura, T. P.; Ramana, M. M. V.; Kudav, N. A. *Synth. Commun.* **1988**, *18*, 2161.

(38) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. S.; Burgin, T. P.; Whitesides, G. W.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(39) Cai, L.; Yao, Y.; Yang, J.; Price, D. W.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 2905.

(40) Spartan version 5.1; 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A.

Scheme 5



the difference between redox peak potentials was increased compared to that of the bare Au electrode (Figure 3a). After a 30 min assembly (Figure 3c), the current was greatly decreased, and the CV showed an almost flattened capacitance shape. After 1 h, the CV indicated that the electrode was fully passivated (Figure 3d), resulting in no electrochemical response at the Au electrode. The passivation of the Au electrode is indicative of SAM formation from compound **4**.

Additional data were gathered using SWE to measure SAM film thicknesses resulting from self-assembly experiments with OPEs **1–6**. Table 1 summarizes the SWE thicknesses and theoretical values of monolayers formed on gold for each target compound. In general, measured values were slightly lower than theoretical ones, although it should be noted that the tilt angle from surface normal was set at 20°.³⁸

Compounds **2**, **3**, **5**, and **6** have thicknesses approaching the theoretical value for complete monolayer formation after 24 h provided consideration for molecular tilt and twist angles.^{41,42} Conversely, compounds **1** and **4** showed larger differences with respect to theoretical values, most likely due to formation of a less ordered SAM or, in the case of **1**, possibly the preference of the molecule to assemble in a zigzag conformation similar

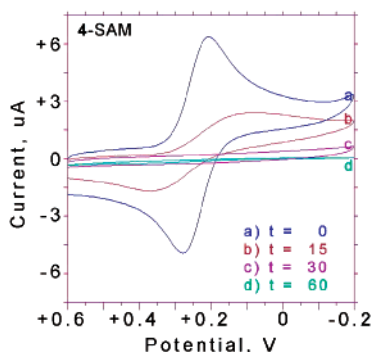
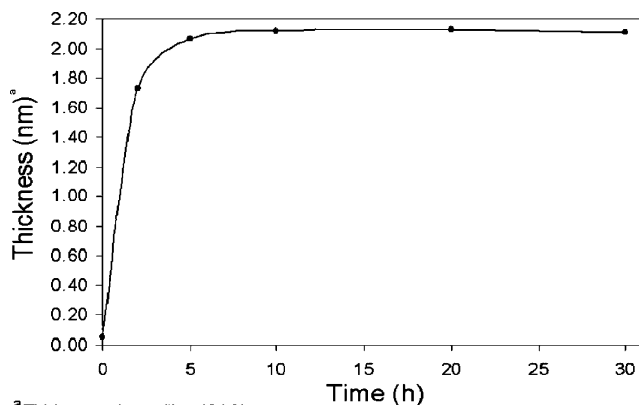


Figure 3. Cyclic voltammograms of SAMs formed with compound **4** on a gold electrode at different self-assembly times: (a) 0 min, (b) 15 min, (c) 30 min, (d) 60 min. A potential was applied to the SAM in aqueous solutions with 1 mM K₃[Fe(CN)₆] and 0.1 M KCl to show the passivation ability of the SAM prepared over the differing time intervals. The scan rate was 0.1 V/s at 23 °C, electrode surface area was 1 cm², and the initial scan direction was negative.

Table 1. Comparison of SWE Results and Theoretical Thicknesses of a 24 h (+5 h at 40 °C) Chemical Assembly of Compounds 1–6 on a Au Substrate^a

compound	experimental thickness (nm) ^b	theoretical thickness (nm) ^c
1	0.9	1.5
2	1.8	2.1
3	1.4	1.6
4	0.9	1.3
5	2.5	2.3
6	2.3	2.3

^a Self-assembly was conducted in a solvent mixture of THF–EtOH (1:1), and the thioacetates were base-deprotected in situ with NH₄OH.³⁸ ^b Values with ± 10% of error. ^c At a 20° to surface normal angle.



^a Thickness values with a 10±% error

Figure 4. Growth kinetics profile of compound **5** assembled on Au in a THF/EtOH/NH₄OH solution.

to the structure represented in Figure 2b. As shown in Figure 4, further ellipsometric analysis was done by recording the growth kinetics of compound **5** while forming a SAM on Au and monitoring the thickness by SWE.

SAM formation was rapid during the first 5 h, then slowed, and reached near-saturated coverage after 10 h. Similar phenomena have been observed in the adsorption kinetics of nitrated OPEs³⁹ and alkanethiols^{43,44}

(41) Dunbar, T. D.; Cygan, M. T.; Bumm, L. A.; McCarty, G. S.; Burgin, T. P.; Reinert, W. A.; Jones, L.; Jackiw, J. J.; Tour, J. M.; Weiss, P. S.; Allara, D. L. *Phys. Chem. B* **2000**, *104*, 4880.

(42) Stapleton, J. J.; Harder, P.; Daniel, T. A.; Reinard, M. D.; Yao, Y.; Price, D. W.; Tour, J. M.; Allara, D. L. *Langmuir* **2003**, *19*, 8245.

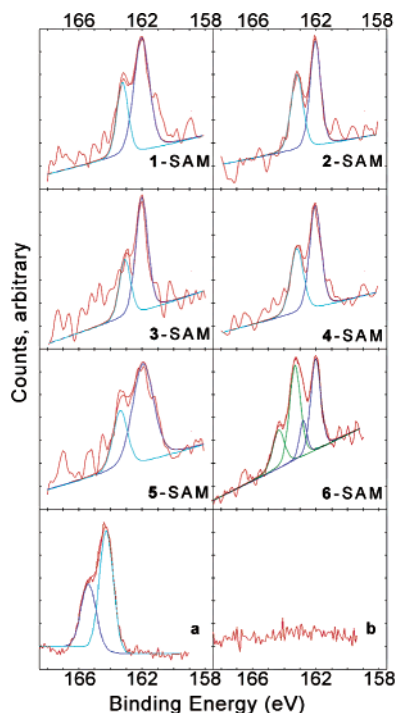


Figure 5. High-resolution XPS multiplex for the S(2p) region of SAMs on Au of compounds **1–6** assembled for 24 h. For comparison, the signals shown in **a** are from oligomer **2** as the unreacted solid, and inset **b** is from a cleaned, bare Au sample with no SAM formed. Deconvolutions were made for the spin-orbit components S(2p^{3/2}) and S(2p^{1/2}) peaks. For the **6**-SAM note that the deconvoluted doublet signal for the S(2p) of the unreacted **6** thioacetate is shown in green, while the doublet signal for the S(2p) of the **6** thiolate on Au is shown in blue. Comparison of the two doublets indicates there is a ~1:1 mixture of unreacted thioacetate to the thiol. XPS pass energy was 11.75 eV in a 45° takeoff angle. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.

on a Au surface. While alkanethiols show a faster film formation (1–2 min), the data in Figure 4 are in agreement with the assembly times reported for OPEs.³⁹

The chemical integrity at the interface level of the SAMs was verified by XPS. Figure 5 shows multiplex spectra of the S(2p) region of the SAMs formed on Au using compounds **1–6**.

Similarly, Figure 6 summarizes high-resolution XPS signals at the C(1s) region for the same SAMs.

High-resolution XPS multiplex of unreacted solids for S(2p) from the thioacetates of oligomers **1–6** were also recorded, and the corresponding signal for compound **2** is included in Figure 5 inset **a** for comparison purposes. For all unreacted solids, binding energies for S(2p^{1/2}) were about 2 eV higher than their corresponding SAMs. The signals for sulfur species, assigned at 162 and 163 eV,⁴² corresponding to the Au–S-oligomer bonding present in the SAM for every compound (Figure 5) was evidence for direct attachment of these oligomers to the Au surface. It is worth noting that the S(2p) signals for SAMs of compounds **4–6** showed small amounts of other sulfur species such as thioacetates or thiols from unreacted oligomer that did not undergo surface attachment.

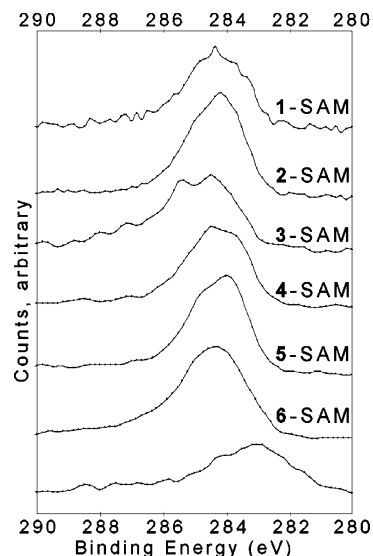


Figure 6. High-resolution XPS multiplex for the C(1s) region of SAMs on Au of compounds **1–6**. The bottom profile corresponds to a bare Au sample with no SAM formed. XPS pass energy was 11.75 eV in a 45° takeoff angle. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.

The SAM formed with compound **6** showed signals for both the SAM thiolate (in blue in the **6** SAM spectrum) and higher energy unreacted thioacetate (in green in the **6**-SAM spectrum) in a ratio ~1:1,⁴⁵ indicating incomplete SAM formation (Figure 5). Longer assembly times might improve the overall quality of the monolayer.⁴² These assignments fit well with the literature precedent from arylthiolate⁴² and alkanethiolate⁴⁶ monolayers on gold. Binding energies and relative concentrations for nitrogen, carbon, and sulfur species are summarized in Table 2. The difference in binding energies for unreacted thioacetate and the thiolate covalently attached to the Au surface is evident by comparing entries **1–6** corresponding to the different SAMs and entry **7** corresponding to the unreacted solid oligomer **6**. The binding energy of 406.1 eV for an electron-deficient nitrogen species corresponds to the nitro group present on compounds **3** and **6**.

The C(1s) signal at 284.6 ± 0.2 eV is assigned to carbon of **1–6** and is different from carbon contamination observed in a bare Au sample with no SAM formed (Figure 6).

5. Summary

We report a new class of structurally isomorphic U-shaped OPEs containing two alligator clips that are capable of forming monolayers on Au surfaces. The quality of this process was analyzed by different techniques. SWE showed near-complete SAM formation after 10 h on a Au surface. Complete SAM formation was also observed on a working Au electrode monitored by CV when applying a potential in aqueous solution. XPS showed that the U-shaped oligomers produced chemisorbed SAMs with clear evidence for Au–S bond formation. Dihedral angle calculations for the terphenyl

(43) Bain, C. D.; Troughton, E. B.; Tao, Y. Y.; Evall, J.; Whitesides, G. W.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(44) Benisebaa, F.; Voicu, R.; Huron, L.; Ellis, T. H. *Langmuir* **1996**, *13*, 5335.

(45) SAM formation for compound **6** did not include the final 5 h assembly at 40 °C.

(46) Laibinis, P. E.; Whitesides, G. W.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

Table 2. Binding Energies and Relative Concentrations for N, C, and S Species Observed by XPS on SAMs Formed with Each Compound^a

entry	compound	binding energy (eV) ^b				relative concentration (%) ^c		
		N(1s)	C(1s)	S(2p ^{3/2})	S(2p ^{1/2})	C(1s)	S(2p)	N(1s)
1	1-SAM		284.6	163.28	162.04	57.7	3.1	
2	2-SAM		284.4	163.18	162.05	68.1	1.1	
3	3-SAM	406.1	284.8	163.12	162.18	52.1	3.3	6.7
4	4-SAM		284.6	163.22	162.06	44.0	3.8	
5	5-SAM		284.4	163.43	162.07	55.4	3.8	
6	6-SAM	406.1	284.8	163.36	162.03	64.7	1.5	2.5
7	6	406.1	284.4	164.45	163.40	95.2	2.8	3.4

^a SAM formation was in a solution of THF/EtOH/NH₄OH for 24 h. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs. ^b Values with ± 0.2 eV of error. ^c Values with $\pm 2\%$ of error. For entries 1–6 Au comprised the remainder of the measured elements.

core of **2** showed that there are two energy minimized conformations, one in which both alligator clips would be situated for attachment to the same Au surface while in the other the two alligator clips would be about 90° apart, possibly leading to incomplete SAM formation. The anthracene-based oligomers showed higher amounts of unreacted thioacetate in the XPS, probably due to a lower solubility and the need for longer self-assembly times than we used. The results of this molecule–metal interface analysis has encouraged us to pursue microscopy studies, a work currently in progress, with the aim of developing a better understanding of the role of these two classes of OPEs as future candidates for molecular electronics testing and development.

6. Experimental Section

6.1. Calculations. Total energies and energy minimizations of molecular structures were calculated using Spartan 5.1.⁴⁰ The oligomers structures were geometry minimized at the parametric method No. 3 (PM3) level previous to a full optimization at the density functional theory (DFT) level.

6.2. Gold Substrates. Gold films were deposited by thermal evaporation of 200 nm thick Au onto Si wafers with a 25 nm Cr adhesion layer at a rate of 1 Å/s at 2×10^{-6} Torr. Before use, the Au substrates were cleaned by a UV/O₃ cleaner (Boekel Industries, Inc., Model 135500) for 10 min in order to remove organic contamination and submerged in ethanol for 10 min before being dried in flowing N₂. This procedure was used to provide a reproducibly clean Au surface.^{47,48}

6.3. Self-Assembly. The oligomer (1 mg) was dissolved in a solution of THF (3 mL) and EtOH (3 mL). Concentrated NH₄OH (10 μ L) was then added, and the mixture was incubated for 10 min at room temperature in order to deprotect the thiol group. The cleaned Au substrates were immersed into the adsorbate solution at room temperature for a period of 24 h, followed by 5 h at 40 °C, unless otherwise stated. All the solutions were freshly prepared, previously purged with N₂ for an oxygen-free environment, and kept in the dark during immersion to avoid photooxidation. After assembly, the samples were removed from the solution, rinsed thoroughly with EtOH, and blown dry with N₂.

6.4. SWE Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single wavelength (632.8 nm laser) Gaertner Stokes Ellipsometer. The n_s and k_s values were recorded for every clean Au sample and used for their corresponding SAM-adsorbed sample. The refractive index was $n_f = 1.55$ for all compounds ($k_f = 0$).³⁸

6.5. CV Monitored Electrode Passivation. The electrochemistry experiments were carried out using a BAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc). A conventional three-electrode cell was used with a gold substrate as the working electrode with surface area of 1 cm², a platinum wire as the counter electrode, and a Ag/AgNO₃ (10 mM AgNO₃ and 0.1 M Bu₄NBF₄ in acetonitrile) as the reference electrode. The scan rate was 0.1 V/s at 23 °C, and the initial scan direction was negative. Self-assembly on the working electrode

was performed in an organic solution of 1 mM of the corresponding oligomer and base. After self-assembly for the designated time, samples were removed from the solutions and rinsed with EtOH.

6.6. XPS Measurements. A Physical Electronics (PHI 5700) XPS/ESCA system at 3×10^{-9} Torr was used to take photoelectron spectra. A monochromatic Al X-ray source at 350 W was used with an analytical spot size of 800 μ m and 45° takeoff angle, with a pass energy of 11.75 eV. The Au(4f) binding energy of 84.00 eV was taken as a reference for all SAMs.

6.7. Material and General Procedures. Unless stated otherwise, reactions were performed in an oven-dried, nitrogen flushed glassware equipped with a magnetic stir bar and using freshly distilled solvents. Reagent grade diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Toluene (PhMe) and triethylamine (TEA) were distilled from calcium hydride. Reagent grade *n*-hexanes, methylene chloride (CH₂Cl₂), methanol (MeOH), ethanol (EtOH), and ethyl acetate (EtOAc) were used without further distillation. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25-mm). In general, the chromatography guidelines reported by Still were followed.⁴⁹ Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230–400 mesh). ¹H and ¹³C NMR spectra were observed at 400 and 100 MHz, respectively, on a Bruker Avance 400 spectrometer. NMR chemical shifts values for deuterated solvents were followed as reported.⁵⁰ IR spectra were obtained on a Nicolet Avatar 360 FTIR. Mass spectroscopy was performed at the Rice University Mass Spectroscopy Laboratory. Melting point values are uncorrected. All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

6.8. General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium–Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).³² To a screw cap tube or a round-bottom flask were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol % based on aryl halide), and copper(I) iodide (10 mol % based on aryl halide). Alternatively, a mixture of bis(dibenzylideneacetone)palladium(0) (10 mol % based on aryl halide) and triphenyl phosphine (10 mol % based on aryl halide) was used. The vessel was sealed with a rubber septum, evacuated, and backfilled with nitrogen (3 \times). A cosolvent of THF was added followed by the amine base. The terminal alkyne was then added followed by replacing the septum with a screw cap and the reaction was heated if necessary. TLC was used to follow the progress of the reaction, and when complete, the reaction vessel was cooled to room temperature,

(47) Ron, H.; Matlis, S.; Rubinstein, I. *Langmuir* **1998**, *14*, 1116.

(48) Ron, H.; Rubinstein, I. *J. Am. Chem. Soc.* **1998**, *120*, 8486.

(49) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

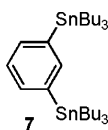
(50) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

and the mixture was quenched with water or a saturated solution of NH_4Cl . The organic layer was diluted with organic solvent and washed with brine ($3\times$). The combined aqueous layers were extracted with organic solvent ($3\times$), and the combined organic layers were dried over anhydrous MgSO_4 , the slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

6.9. General Procedure for the Coupling of a Trialkylaryl Stannane with an Aryl Halide Utilizing a Palladium(0) Cross-Coupling (Stille Protocol).³⁰ To a screw cap tube or a round-bottom flask were added the aryl halide, the stannane, and a mixture of bis(dibenzylideneacetone)-palladium(0) (10 mol % based on aryl halide) and triphenylarsine (20 mol % based on aryl halide). Alternatively, tetrakis(triphenylphosphine)palladium(0) (10 mol % based on aryl halide) was used. The vessel was then sealed with a rubber septum, evacuated, and backfilled with nitrogen ($3\times$). THF was added, and the reaction was heated at 75°C (after capping with a screw cap if a tube was used). The reaction vessel was cooled to room temperature, and the mixture was quenched with water and extracted with organic solvents ($3\times$). The combined organic layers were dried over anhydrous MgSO_4 , the slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

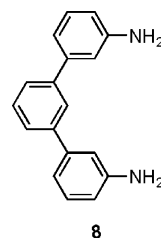
6.10. General Procedure for Alkaline Deprotection of Trimethylsilyl-Protected Alkynes. The TMS-protected alkyne was added to an open round-bottom flask, and a solution of K_2CO_3 in MeOH was added to dissolve the organic compound. The reaction was monitored by TLC every 5 min until deprotection was complete. The reaction was quenched with water and extracted with organic solvents ($3\times$). The combined organic layers were dried over anhydrous MgSO_4 , the slurry was filtered, and the solvent was removed from the filtrate in vacuo to provide a crude product for further purification via flash chromatography.

6.11. General Procedure for Iodination of Anilines via Diazotization.³¹ Into a round-bottom flask inside a glovebox was added NOBF_4 (1.1 equiv per mole of aniline). CH_3CN was then added to dissolve the salt, and the solution was cooled to -30°C . Into a separate round-bottom flask was added the aniline dissolved in CH_3CN and/or THF. The aniline solution was transferred dropwise via cannula into the NOBF_4 solution, and the temperature was allowed to rise to 0°C . Et_2O was then slowly added until a precipitate formed. The solid product was filtered, and the filter cake was washed with Et_2O ($3\times$) and dried in vacuo. As an alternative procedure, NOBF_4 was replaced by $\text{BF}_3\cdot\text{Et}_2\text{O}$ (4 equiv per mole of aniline), and the aniline dissolved in CH_3CN and/or THF was added dropwise to the boron trifluoride etherate. After 30 min, an alkyl nitrite (3.5 equiv per mole of aniline) was then added to the reaction. In either case, the resulting aryldiazonium tetrafluoroborate was filtered and slowly added as the isolated solid into a mixture of NaI (2 equiv per mole of diazonium salt) and I_2 (1.5 equiv per mole of diazonium salt) dissolved in CH_3CN . After 30 min, the reaction mixture was dissolved in CH_2Cl_2 , and a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added until the dark color disappeared. The organic layer was washed with water, and the aqueous phase was extracted with CH_2Cl_2 . The organic layers were combined and dried over MgSO_4 , and the slurry was filtered, followed by removal of the solvent from the filtrate in vacuo for further purification.

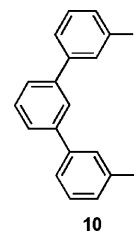


6.11.1. 1,3-Bis(tributylstannyl)benzene (7). Into a 500 mL round-bottom flask was added 1,3-dibromobenzene (30.0 g, 127.1 mmol) dissolved in THF (100 mL) before cooling to -78°C . $t\text{-BuLi}$ (234 mL, 255.5 mmol) was added dropwise from an attached addition funnel, and the reaction mixture was

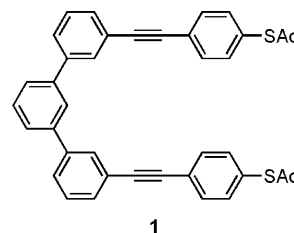
stirred for 45 min before adding dropwise tri-*n*-butyltin chloride (74 mL, 267 mmol). The reaction was allowed to warm to room temperature before being quenched with water (100 mL) and extracted with Et_2O (100 mL), and the organic layer was dried over MgSO_4 . Removal of the solvent in vacuo and Kugelrohr distillation (140°C at 0.25 mmHg) resulted in the removal of starting material and monoadduct. The remaining clear oil was then purified by flash chromatography (hexanes), affording the desired product (33.0 g, 70% yield): IR (neat) 2957, 2732, 2630, 2353, 1874, 1674, 1551, 1456, 1371, 1288, 1253, 1182, 1076, 1007 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (m, 1H), 7.47 (m, 2H), 7.37 (m, 1H), 1.61 (m, 12H), 1.42 (m, 12H), 1.12 (m, 12H), 0.94 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 141.6, 136.2, 128.0, 29.3, 27.6, 13.8, 9.8; HRMS calcd for $\text{C}_{30}\text{H}_{58}\text{Sn}_2$ 658.2582, found 658.2591.



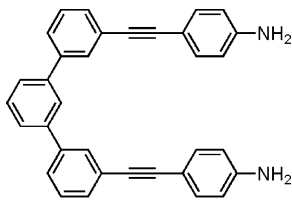
6.11.2. 3,3'-Diamino-[1,1':3,1'']terphenyl (8). Following the Stille coupling protocol, **7** (5.0 g, 7.6 mmol), $\text{Pd}(\text{dba})_2$ (0.3 g, 0.3 mmol), AsPh_3 (0.4 g, 0.6 mmol), and 3-iodoaniline (3.3 g, 15.2 mmol) were dissolved in THF (40 mL). The reaction was stirred for 20 h at 75°C . Purification by flash chromatography (4:1, hexanes:EtOAc) yielded the desired adduct (1.2 g, 31% yield) as a brown oil: IR (neat) 3471, 3390, 3020, 2401, 1612, 1520, 1471, 1415, 1216, 1039 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (m, 1H), 7.49 (m, 3H), 7.25 (m, 4H), 6.96 (dd, $J = 7.6, 0.8$ Hz, 1H), 6.86 (s, 1H), 6.71 (dd, $J = 7.6, 0.8$ Hz, 1H), 3.71 (br s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 143.6, 140.9, 130.2, 129.9, 125.8, 122.8, 117.5, 114.7, 113.8; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2$ 260.1313, found 260.1308.



6.11.3. 3,3'-Diiodo-[1,1':3,1'']terphenyl (10). Following the general iodination procedure via diazotization, **8** (4.0 g, 15.3 mmol) dissolved in THF (5 mL) was added to $\text{BF}_3\cdot\text{Et}_2\text{O}$ (15.5 mL, 123 mmol) followed by the addition of isoamyl nitrite (14.3 mL, 107.5 mmol). After the precipitate was isolated, a solution of NaI (6.3 g, 42.4 mmol) and I_2 (8.0 g, 31.8 mmol) in CH_3CN (50 mL) was added. Flash chromatography (2:1, hexanes:Et₂O) gave the desired product (4.4 g, 60% yield over two steps) as a light yellow oil: IR (neat) 3681, 3018, 2401, 1942, 1873, 1761, 1688, 1581, 1555, 1462, 1422, 1388, 1215, 1080, 1031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (m, 2H), 7.69 (m, 3H), 7.51 (m, 2H), 7.45 (m, 1H), 7.31 (m, 2H), 7.18 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 136.9, 136.1, 130.9, 130.6, 130.5, 130.2, 126.4, 125.8, 123.1; HRMS calcd for $\text{C}_{18}\text{H}_{12}\text{I}_2$ 481.9028, found 481.9025.

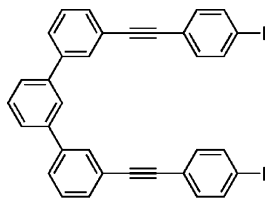


6.11.4. Thioacetic Acid S-[4-[3-(4-acetylsulfanylphenylethynyl)-[1,1';3',1'']terphenyl-3''-ylethynyl]phenyl] Ester (1). Following the Sonogashira coupling protocol, **10** (500 mg, 1.00 mmol), **11**⁵¹ (384 mg, 2.10 mmol), PdCl₂(PPh₃)₂ (73 mg, 0.10 mmol), and CuI (40 mg, 0.20 mmol) were dissolved in THF (10 mL) and TEA (1.2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1, hexanes:Et₂O) afforded the desired product (150 mg, 26% yield) as a light yellow solid: mp 82–86 °C; IR (KBr) 3059, 1697, 1696, 1558, 1473, 1424, 1385, 1348, 1256, 1118, 1003 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (m, 3H), 7.60 (m, 4H), 7.52 (m, 6H), 7.43 (m, 5H), 7.31 (m, 2H), 2.45 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 193.3, 142.3, 139.9, 134.3, 132.2, 131.0, 130.4, 130.1, 129.0, 128.3, 127.3, 125.7, 124.3, 123.6, 123.0, 90.8, 89.2, 30.3; HRMS calcd for C₃₈H₂₆O₂S₂ 578.1374, found 578.1355.



13

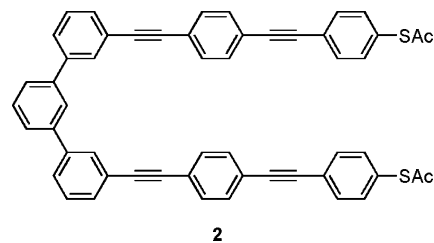
6.11.5. 3,3''-Bis-*p*-anilineethynyl[1,1';3',1'']terphenyl (13). Following the Sonogashira coupling protocol, **10** (3.4 g, 7.50 mmol), **12**³³ (1.8 g, 15.80 mmol), PdCl₂(PPh₃)₂ (530 mg, 0.70 mmol), and CuI (290 mg, 0.50 mmol) were dissolved in THF (30 mL) and TEA (8.4 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1, hexanes:Et₂O) afforded the desired product (3.0 g, 87% yield) as a brown oil: IR (neat) 3471, 3377, 3046, 2199, 1594, 1513, 1468, 1292, 1222, 1173 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (m, 2H), 7.71 (m, 2H), 7.52 (m, 6H), 7.50 (m, 5H), 7.30 (m, 1H), 6.65 (m, 4H), 3.85 (br s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 142.7, 139.9, 133.2, 130.8, 130.6, 130.5, 130.3, 130.1, 129.0, 126.5, 125.9, 124.7, 123.1, 114.9, 90.8, 87.2; HRMS calcd for C₃₄H₂₄N₂ 460.1939, found 460.1934.



15

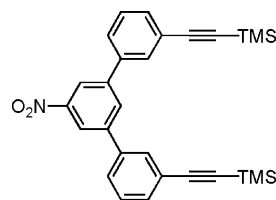
6.11.6. 3,3''-Bis-(4-iodophenylethynyl)-[1,1';3',1'']terphenyl (15). Following the general iodination procedure via diazotization, **13** (2.6 g, 5.7 mmol) was dissolved in CH₃CN (10 mL) and added to a solution of NOBF₄ (1.4 g, 12.0 mmol) in CH₃CN (5 mL). The resulting aryldiazonium tetrafluoroborate **14** was added to a solution of NaI (2.4 g, 14.4 mmol) and I₂ (2.7 g, 10.8 mmol) in CH₃CN (15 mL). Flash chromatography (2:1, hexanes:Et₂O) gave the desired product (2.3 g, 88% yield over two steps) as a pale white powder: mp 73–77 °C; IR (KBr) 3429, 3056, 1559, 1474, 1382, 1251, 1046 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (m, 4H), 7.72 (m, 4H), 7.53 (m, 5H), 7.43 (m, 1H), 7.32 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.2, 140.0, 137.6, 133.1, 130.9, 130.6, 130.4, 130.2, 129.0, 127.2, 125.7, 123.6, 123.1, 122.6, 94.5, 90.7; HRMS calcd for C₃₄H₂₀I₂ 681.9654, found 681.9612.

6.11.7. Thioacetic Acid S-[4-(4-{3''-[4-(4-Acetylsulfanylphenylethynyl)phenylethynyl]-[1,1';3',1'']terphenyl-3''-ylethynyl]phenylethynyl]phenyl] Ester (2). Following the Sonogashira coupling protocol, **15** (250 mg, 0.37 mmol), **11**⁵¹ (1.8 g, 15.8 mmol), PdCl₂(PPh₃)₂ (52 mg, 0.7 mmol), and CuI (28 mg, 0.14 mmol) were dissolved in THF (40 mL) and TEA (0.4 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1, hexanes:



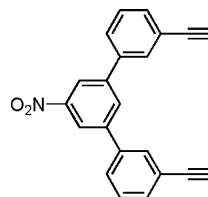
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Et₂O) afforded the desired product (165 mg, 58% yield) as a light brown solid: mp 258–262 °C; IR (KBr) 3020, 2400, 1702, 1594, 1508, 1473, 1426, 1214, 1114 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 6.4, 4H), 7.55 (m, 16H), 7.43 (m, 6H), 7.41 (m, 2H), 2.46 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 193.6, 142.5, 140.1, 134.4, 132.3, 131.8, 131.1, 130.8, 130.5, 130.3, 129.2, 128.5, 127.4, 125.9, 124.4, 123.8, 123.4, 123.1, 123.0, 91.2, 90.9, 90.7, 89.6, 30.5; HRMS calcd for C₅₄H₃₄O₂S₂ 778.2000, found 778.2011.



17

6.11.8. 5'-Nitro-3,3''-bistrimethylsilanylethynyl-[1,1';3',1'']terphenyl (17). Following the Stille coupling protocol, 1,3-dibromo-5-nitrobenzene (6.7 g, 24.0 mmol), **16**³⁴ (22.2 g, 48.0 mmol), and Pd(PPh₃)₄ (2.7 g, 2.4 mmol) were dissolved in PhMe (40 mL). The reaction was stirred for 20 h at 75 °C. Purification by flash chromatography (4:1, hexanes:EtOAc) yielded the desired adduct (5.0 g, 45% yield) as a brown oil: IR (neat) 3088, 2959, 2859, 2677, 2305, 2159, 1794, 1599, 1535, 1452, 1346, 1335, 1258, 1155, 1100 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 1H), 7.49 (m, 3H), 7.25 (m, 4H), 6.96 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.86 (s, 1H), 6.71 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.71 (br s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 143.6, 140.9, 130.2, 129.9, 125.8, 122.8, 117.5, 114.7, 113.8, 105.2, 94.7, 0.2; HRMS calcd for C₁₈H₁₆N₂ 260.1313, found 260.1308.

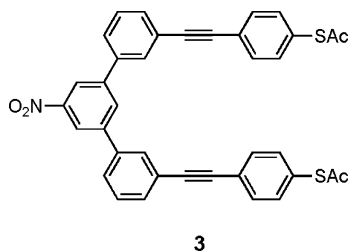


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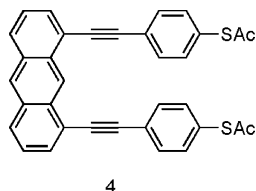
6.11.9. 3,3''-Diethynyl-5'-nitro[1,1';3',1'']terphenyl (18). Following the general deprotection of TMS-alkynes, **17** (5.0 g, 10.7 mmol) was dissolved in a mixture of CH₂Cl₂ (15 mL), MeOH (15 mL), and K₂CO₃ (11.8 g, 85.5 mmol). Flash chromatography (2:1, hexanes:Et₂O) afforded the desired product (3.2 g, 92% yield) as a pale white powder: mp 116–120 °C; IR (KBr) 3281, 3073, 1602, 1530, 1527, 1480, 1343, 1107 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.35 (m, 2H), 8.02 (m, 2H), 7.71 (m, 2H), 7.56 (m, 4H), 7.26 (m, 1H), 3.16 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 137.7, 136.0, 132.8, 130.9, 129.5, 127.6, 125.6, 123.5, 120.8, 82.9, 78.5; HRMS calcd for C₂₂H₁₃NO₂ 323.0946, found 323.0954.

6.11.10. Thioacetic Acid S-[4-[3-(4-Acetylsulfanylphenylethynyl)-[1,1';3',1'']terphenyl-3''-ylethynyl]phenyl] Ester (3). Following the Sonogashira coupling protocol,

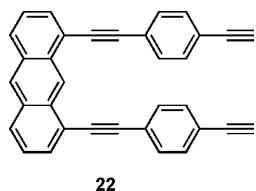
(51) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.; Chen, J.; Wang, W.; Campbell, I. H. *Chem. Eur. J.* **2001**, *7*, 5118.



18 (87 mg, 0.20 mmol), **19**⁵¹ (150 mg, 0.50 mmol), PdCl₂(PPh₃)₂ (19 mg, 0.02 mmol), and CuI (11 mg, 0.05 mmol) were dissolved in THF (10 mL) and TEA (0.3 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (15 mg, 13% yield) as a light brown oil: IR (neat) 3021, 2402, 2204, 1705, 1549, 1365, 1216, 1123 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.37 (m, 4H), 8.04 (m, 2H), 7.75 (m, 2H), 7.59 (m, 2H), 7.55 (m, 5H), 7.48 (m, 2H), 7.41 (m, 4H), 2.44 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 193.4, 149.3, 143.6, 137.7, 136.0, 134.3, 132.3, 130.3, 129.5, 128.6, 127.2, 125.5, 124.3, 123.4, 120.8, 90.2, 89.9, 30.4; HRMS calcd for C₃₈H₂₅NO₄S₂ 623.1225, found: 623.1227.

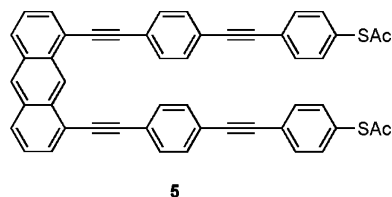


6.11.11. Thioacetic Acid S-[4-[8-(4-Acetylsulfanylphenylethynyl)anthracen-1-ylethynyl]phenyl] Ester (4). Following the Sonogashira coupling protocol, **19**³⁵ (520 mg, 1.88 mmol), **20**³⁶ (200 mg, 0.89 mmol), PdCl₂(PPh₃) (50 mg, 0.08 mmol), and CuI (30 mg, 0.15 mmol) were dissolved in THF (20 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (210 mg, 45% yield): mp 200 °C (decomp); IR (KBr) 1697, 1119, 1093 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.57 (s, 1H), 8.49 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.82 (dd, *J* = 6.0, 0.9 Hz, 2H), 7.59 (d, *J* = 6.4 Hz, 4H), 7.50 (quart, *J* = 6.9, 1.6 Hz, 2H), 7.28 (d, *J* = 6.4 Hz, 4H), 2.48 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 134.6, 132.5, 131.7, 131.6, 131.0, 129.5, 128.5, 127.8, 125.4, 124.6, 124.1, 121.3, 94.3, 89.4, 30.5; HRMS calcd for C₃₄H₂₂O₂S₂ 526.1061, found 526.1063.

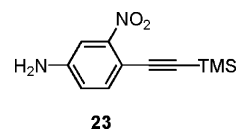


6.11.12. 1,8-Bis-(4-ethynylphenylethynyl)anthracene (22). Combining the Sonogashira coupling protocol and the general deprotection of TMS-alkynes, **20**³⁶ (200 mg, 0.89 mmol), **21**⁵² (550 mg, 1.86 mmol), PdCl₂(PPh₃)₂ (30 mg, 0.04 mmol), and CuI (20 mg, 0.09 mmol) were dissolved in THF (15 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1 hexanes:CH₂Cl₂) afforded a yellow solid that was immediately dissolved in a mixture of MeOH (30 mL), CH₂Cl₂ (30 mL), and K₂CO₃ (960 mg, 7.01 mmol). The reaction was stirred for 6 h. Purification by flash chromatography (2:1 hexane:CH₂Cl₂) afforded the desired product (100 mg, 27% yield) as a yellow solid: mp 240 °C (decomp); IR (KBr) 3296,

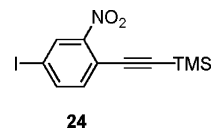
3041, 2923, 2201, 1919, 1637, 1497, 1392, 1336, 1255, 1159, 1097, 1023 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.53 (s, 1H), 8.46 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 6.7 Hz, 2H), 7.49 (m, 6H), 7.37 (d, *J* = 8.5, 4H), 3.23 (s, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 132.4, 131.8, 131.7, 131.6, 131.0, 129.5, 127.8, 125.4, 124.1, 123.8, 122.4, 121.3, 94.5, 89.8, 83.4, 79.3; HRMS calcd for C₃₄H₁₈ 427.1487, found 427.1479.



6.11.13. Thioacetic Acid S-[4-(4-[8-(4-Acetylsulfanylphenylethynyl)phenylethynyl]anthracen-1-ylethynyl)phenylethynyl] Ester (5). Following the Sonogashira coupling protocol, **22** (50 mg, 0.13 mmol), **19**³⁵ (70 mg, 0.26 mmol), Pd(dba)₂ (10 mg, 0.01 mmol), PPh₃ (10 mg, 0.01 mmol), and CuI (10 mg, 0.03 mmol) were dissolved in THF (10 mL) and TEA (1 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (50 mg, 53%) as a yellow solid: mp 248 °C (decomp); IR (KBr) 2921, 2210, 1915, 1689, 1697, 1504, 1391, 1120, 1010 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.60 (s, 1H), 8.51 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 6.4 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 4H), 7.51 (dd, *J* = 6.4, 1.5 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.40 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), 2.46 (s, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 193.5, 134.4, 132.4, 131.98, 131.95, 131.8, 131.7, 130.9, 129.5, 128.5, 127.9, 125.5, 124.4, 124.2, 123.5, 123.2, 121.4, 94.8, 90.9, 90.8, 89.8, 30.5; HRMS calcd for C₅₀H₃₁O₂S₂ 727.1766, found 727.1754.



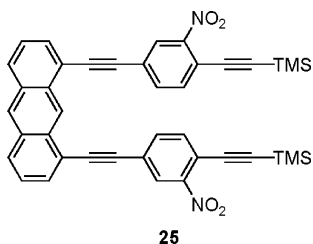
6.11.14. 3-Nitro-4-(trimethylsilyl)ethynylphenylamine (23). Following the Sonogashira coupling protocol, 4-bromo-3-nitroaniline³⁷ (10.0 g, 45.9 mmol), TMSA (7.8 mL, 55.0 mmol), Pd(dba)₂ (1.3 g, 2.3 mmol), PPh₃ (1.2 g, 4.6 mmol), and CuI (0.6 g, 3.2 mmol) were dissolved in THF (200 mL) and TEA (35 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (7.7 g, 71%) as an orange solid: mp 95–99 °C; IR (KBr) 3483, 3379, 2956, 2151, 1621, 1516, 1341, 1317, 846 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.03 (s, 2H), 0.23 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 147.3, 136.3, 118.8, 109.8, 107.4, 100.4, 99.9, 0.0; HRMS calcd for C₁₁H₁₄N₂O₂Si 234.0825, found 234.0826.



6.11.15. 4-Iodo-2-nitrophenylethynyltrimethylsilane (24). Following the general iodination procedure via diazotization, **23** (7.7 g, 32.7 mmol) dissolved in THF (100 mL) was added to BF₃·Et₂O (16.6 mL, 130.9 mmol) followed by the addition of *tert*-butyl nitrite (13.6 mL, 114.5 mmol). After the precipitate was isolated, it was added to a solution of NaI (7.2 g, 48.3 mmol) and I₂ (6.1 g, 24.1 mmol) in CH₃CN (150 mL). Purification by flash chromatography (1:1, hexanes:CH₂Cl₂) afforded the desired product (7.9 g, 69%) as a yellow oil: IR (neat) 2960, 2163, 1545, 1529, 1468, 1342, 1250, 879, 846 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 1.7 Hz, 1H), 7.85 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 0.27 (s,

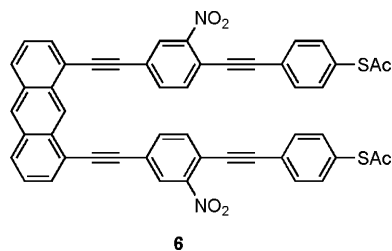
(52) Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*, 5495.

9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 141.7, 136.1, 133.3, 118.0, 105.8, 98.7, 93.0, -0.3 ; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{INO}_2\text{Si}$ 344.9682, found 344.9692.



6.11.16. 1,8-Bis-(3-nitro-4-trimethylsilanylethynylphenylethynyl)anthracene (25). Following the Sonogashira coupling protocol, **20** (350 mg, 1.6 mmol), **24** (1.1 g, 3.3 mmol), $\text{Pd}(\text{dba})_2$ (90 mg, 0.16 mmol), PPh_3 (90 mg, 0.33 mmol), and CuI (60 mg, 0.33 mmol) were dissolved in THF (15 mL) and TEA (3 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (1:1 hexanes: CH_2Cl_2) afforded the desired product (350 mg, 34%) as a yellow solid: mp 157–161 $^\circ\text{C}$; IR (KBr) 2958, 2198, 2158, 1545, 1346, 1246, 863, 843 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.36 (s, 1H), 8.50 (s, 1H), 8.19 (d, $J = 1.7$ Hz, 2H), 8.07 (d, $J = 8.6$ Hz, 2H), 7.85 (dd, $J = 6.9, 0.9$ Hz, 2H), 7.67 (dd, $J = 8.0, 1.7$ Hz, 2H), 7.51 (m, 4H), 0.33 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 135.3, 135.0, 132.2, 131.7, 131.3, 130.3, 128.3, 127.4, 125.5, 124.4, 123.5, 120.4, 118.2, 106.4, 99.3, 92.4, 92.3, -0.1 ; HRMS calcd for $\text{C}_{40}\text{H}_{32}\text{N}_2\text{O}_4\text{Si}_2$ 660.1901, found 660.1906.

6.11.17. Thioacetic Acid S-[4-(4-{8-[4-(4-Acetylsulfanylphenylethynyl)-3-nitrophenylethynyl]anthracen-1-ylethynyl}-2-nitrophenylethynyl)phenyl] Ester (6). Combining the general deprotection of TMS-alkynes and the Sonogashira coupling protocol, **25** (350 mg, 0.53 mmol) was dissolved in a mixture of CH_2Cl_2 (30 mL), MeOH (30 mL), and K_2CO_3 (720 mg, 5.2 mmol), leaving the reaction mixture to



stir for 3 h. Once an orange solid (222 mg) was isolated as the free alkyne, **19** (230 mg, 0.84 mmol), $\text{Pd}(\text{dba})_2$ (20 mg, 0.04 mmol), PPh_3 (20 mg, 0.08 mmol), and CuI (20 mg, 0.08 mmol) were added and dissolved in THF (20 mL) and TEA (2 mL). The reaction was stirred overnight at room temperature. Purification by flash chromatography (CH_2Cl_2) afforded the desired product (150 mg, 35%) as a yellow solid: mp 204–208 $^\circ\text{C}$; IR (KBr) 2212, 1700, 1540, 1520, 1501, 1343, 1113, 1088, 828 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.46 (s, 1H), 8.54 (s, 1H), 8.26 (d, $J = 1.5$ Hz, 2H), 8.10 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 6.9$ Hz, 2H), 7.66 (dd, $J = 8.0, 1.5$ Hz, 2H), 7.51 (m, 8H), 7.28 (d, $J = 8.6$ Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 149.5, 135.4, 134.8, 134.3, 132.8, 131.7, 131.6, 131.5, 130.3, 129.7, 128.2, 127.7, 125.5, 124.2, 123.7, 123.4, 120.4, 118.3, 98.6, 92.5, 92.2, 86.3, 30.6.

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