Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3131–3156

TETRAHEDRON

Biphenyl- and fluorenyl-based potential molecular electronic devices

David W. Price, Jr. and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main St., Houston, TX 77005, USA

Received 16 January 2003; revised 1 March 2003; accepted 1 March 2003

Abstract—New potential molecular electronics devices have been synthesized based on our knowledge of systems that we previously studied. Research has shown that simple molecular systems demonstrate negative differential resistance (NDR) and memory characteristics. The new molecules rely primarily on the redox properties of the compounds to improve upon the solid-state characteristics already observed. Electrochemical tests have been performed in order to evaluate the redox properties with the hope that the electrochemical results can be used as a predictive tool to evaluate the usefulness of those compounds in device configurations. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Molecular electronics is currently a topic of considerable interest among a diverse community of scientists and engineers as well as the general population and popular press.[1] Much effort and capital has been expended to improve and further miniaturize the components of computers. The methods currently used to make the microchips have been commercially scaled down to 0.13 μm (130 nm) feature size (interconnect metal line width, for instance). The lower limit is expected to be about 30 nm.[2] Experts in the semiconductor field estimate that this limit will be reached in 10–15 years.[2b]

If electronics and computer components are to continue decreasing in size beyond the 30 nm limit, new technologies must be invented and explored. Molecular scale devices seem to be a logical approach to reduce the size of current electronic devices. A typical organic 'molecular wire' synthesized in our laboratory is about 2.5 nm long and 0.3 nm wide, 10 times smaller in width than the presumed ultimate 30 nm width of metal lines in solid-state-based devices. Present day personal computers utilize components that contain approximately 10^7 transistors per cm^2. Self-assembled monolayers (SAMs) of molecular scale wires can achieve ordering of approximately 10^{14} molecules/cm^2, seven orders of magnitude greater. Also, one can manufacture one mole of these molecules in a large laboratory flask, which amounts to 6×10^{23} devices, or more than the number of transistors ever made in the history of the world.

Keywords: molecular electronics; biphenyl; fluorenyl.

* Corresponding author. Tel.: +1-7133486246; fax: +1-7133486250; e-mail: tour@rice.edu

It is for these reasons and others that work continues to develop molecular electronics candidates. Of course, there are numerous problems that will need to be solved before molecular computing will be realized, including addressing single molecules in circuits and the need for heat dissipation at these packing levels.[3]

Many molecular structures have been synthesized for use as molecular devices, including switches, wires, controllers, and gates.[4,5] Molecules in the oligo(phenylene ethynylene) (OPE) class having a negative differential resistance (NDR) effect were discovered when nitro-bearing OPE molecules were tested. The defining characteristic of NDR is that the device will only carry significant current in a narrow voltage range. When sandwiched between metal contacts, both the nitro-amino containing compound **1**[6] and the mono-nitro compound **2**[7,8] were shown to demonstrate this NDR effect (Fig. 1).

One proposed mechanism for the NDR effect involves the reduction of the molecules. It was thought that the 'turn-on' voltage, that is, the potential where current began to increase dramatically, was the result of a single-electron reduction of the molecules. The 'turn-off' voltage, where the current essentially stopped, occurred because of a second single-electron reduction. In an effort to understand the mechanism behind the NDR effect, calculations[9] and cyclic voltammetric measurements[10] on the nitro-only compound **2** and its derivatives were performed, both of which are generally in good agreement. In addition, both **1** and **2** demonstrate molecular dynamic random access memory (molecular DRAM).[11] That is, the nanopore devices containing either of these compounds can store conductive states that differ enough from one another to be recognizable. This

doi:10.1016/S0040-4020(03)00334-X

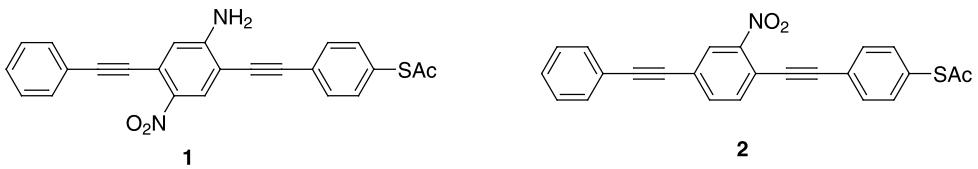


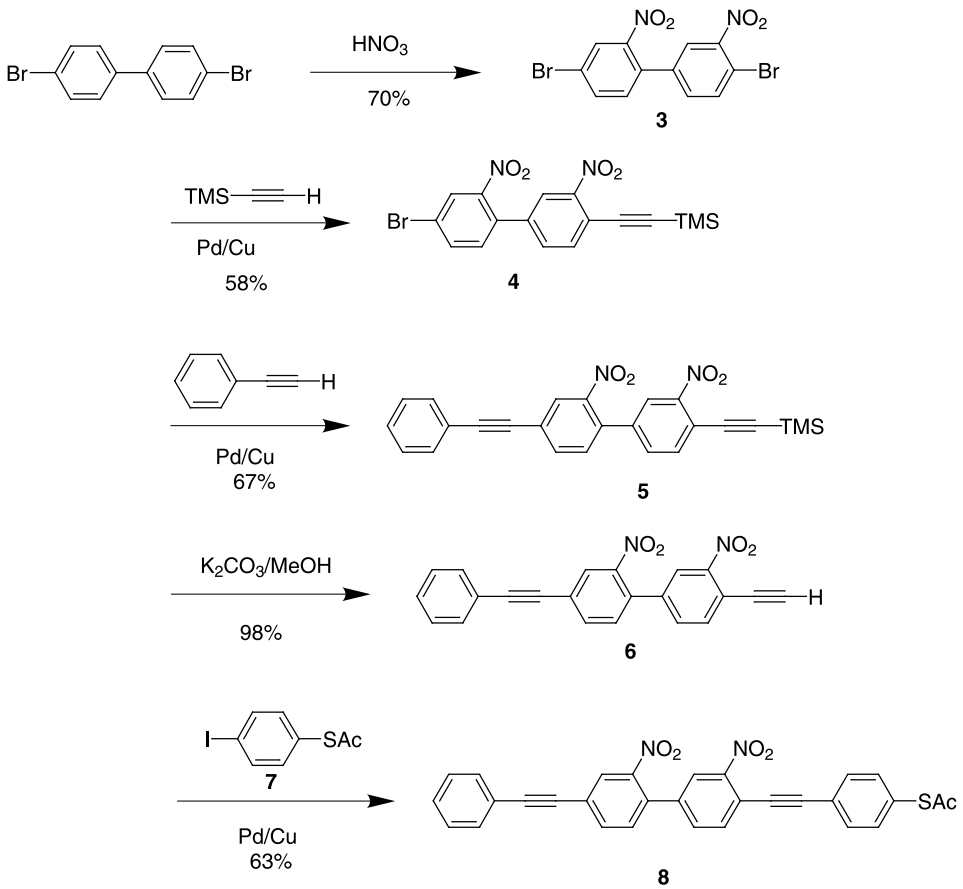
Figure. 1. Both the nitro-amino functionalized OPE **1** and the nitro functionalized **2** demonstrated the NDR effect.

essentially constitutes DRAM as used in modern computers, an interesting achievement. To fully develop the structure–activity relationship (SAR) among this class of compounds, we designed and synthesized a number of compounds that structurally differed from **1** and **2**. We report on those syntheses in this paper.

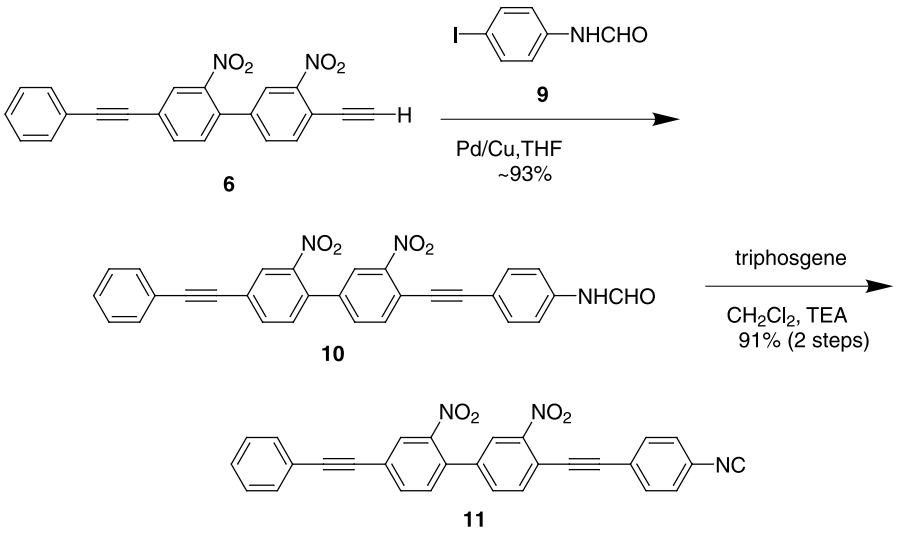
2. Biphenyl cores: synthesis of 2,3′-dintro system

Scheme 1 shows the complete synthesis of a 2,3′-dinitrobiphenyl system. Preliminary data indicate that this compound shows a well-defined room temperature NDR as well as long-term (hours) memory.[12] 4,4′-Biphenyl was nitrated using the conditions of Shaw and Turner[13] to give the 2,3′-dinitro product **3**. By literature precedent and by our own ^{1}H NMR analysis of the crude product mixture, there was approximately 85% of the desired product and 15% of the 2,2′-dinitro product. Recrystallization from ethanol/acetone would only allow for isolation of 70% of pure **3**. Although the 2,2′-product is useful and is currently being used in making a device, it is obtained in higher yields through an alternative method and therefore not isolated here.

Coupling of **3** with 4-ethynyl-1-benzenethioacetate afforded monocoupled product (not shown) in low 14% yield. This has been a problem common to many couplings of nitro-containing compounds with thioacetate-containing alligator clip molecules (molecules bearing moieties that adhere to metal surfaces[3]). Coupling of compound **3** with trimethylsilylacetylene (TMSA) afforded **4** in a modest yield. Coupling of **4** with phenylacetylene provided **5** in a higher yield. Coupling of nitro compounds can be problematic because of the potential for intramolecular reaction between the nitro group and an adjacent alkyne to form cyclic isatogens, as seen by Rosen and coworkers.[14] Lower temperatures and shorter reaction times as well as the use of lower concentrations of base help to reduce or prevent such side reactions. Deprotection of the alkyne using potassium carbonate and methanol afforded **6** in high yield. Coupling of the terminal alkyne with the alligator clip **7** afforded final product **8** in good yield.



Scheme 1. Synthesis of 2,3′-dinitrobiphenyl system **8**.



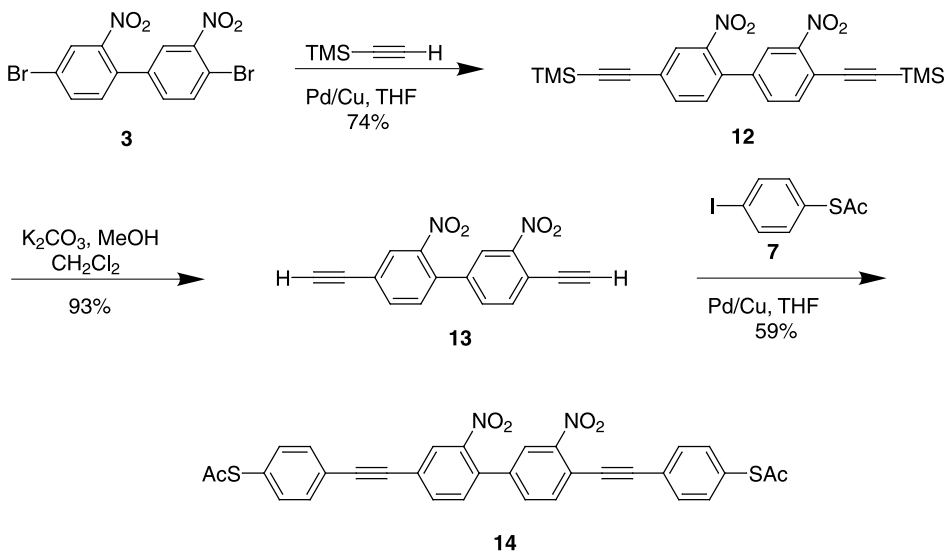
Scheme 2. Synthesis of isonitrile **11**.

The 2,3′-dinitro biphenyl compound **8** shows NDR behavior similar to the mono-nitro and nitro-amino devices **1** and **2**. However, **8** shows an NDR effect that is far more pronounced at room temperature that the NDR effect of **1** or **2**.[7] This supports our theory that the nitro group functionality plays a key role in the NDR switching mechanism and memory effects. A full account of the electrical characteristics will be published separately.

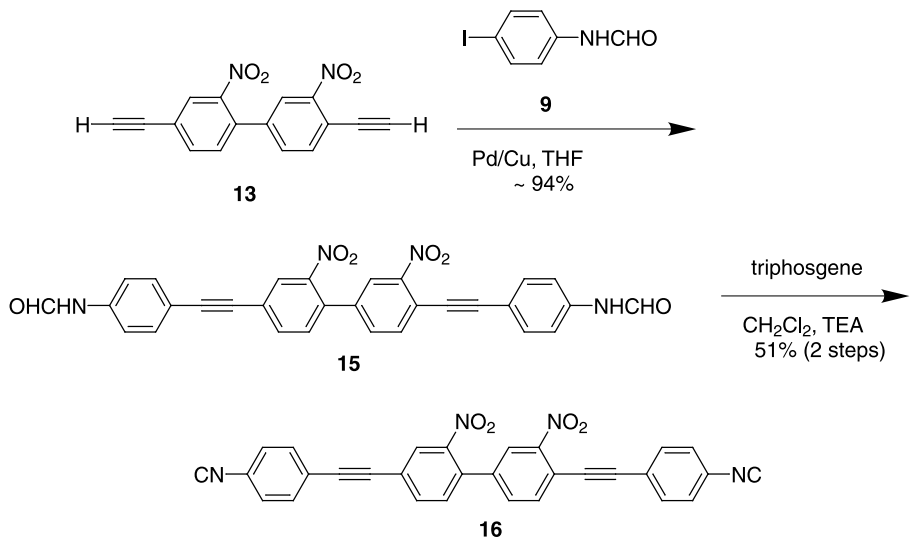
2.1. Biphenyl systems with one or two thioacetyl or isonitrile alligator clips

We are exploring the use of isonitriles as alligator clips for attaching these compounds to metal surfaces. Isonitriles form weaker bonds to gold and other metal substrates than thiols; weaker chemisorption might make for a better alligator clip and thereby better conduction due to changes in the molecular orbital overlap with the Fermi level of the metal. Also, the SAMs that are formed using isonitriles may be more perpendicular to the surface than thiol-based compounds, which might allow for better conduction due to higher delocalization within the molecular system and better overlap of the molecular orbitals with the metals' Fermi levels.[3] Scheme 2 shows the synthesis of the 2,3′-dinitrobiphenyl device synthesized with an isonitrile alligator clip. 4′-Ethynyl-2,3′-dinitro-4-phenylethynyl-biphenyl (**6**) was coupled with formamide **9** to provide **10**. The exact yield was not determined since ^{1}H NMR analysis showed some impurities. In addition, slow rotation about the formamide C–N bond, on the NMR time scale, due to its partial double bond character (tautomerization),[15] produced complex absorbances that made it difficult to assign peaks in the ^{1}H NMR. Compound **10** was dehydrated using triphosgene to provide **11** in a yield of 91% over the two steps.

Scheme 3 shows the complete synthesis of the 2,3′-dinitrobiphenyl compound with two alligator clips. Compound **3** was coupled with an excess of TMSA at room temperature to provide **12** in good yield. If the reaction was heated to 45°C for only a few hours, the yield was reduced, possibly due to cyclization between the 3′-nitro group and



Scheme 3. Synthesis of **14** containing two protected thiol alligator clips.

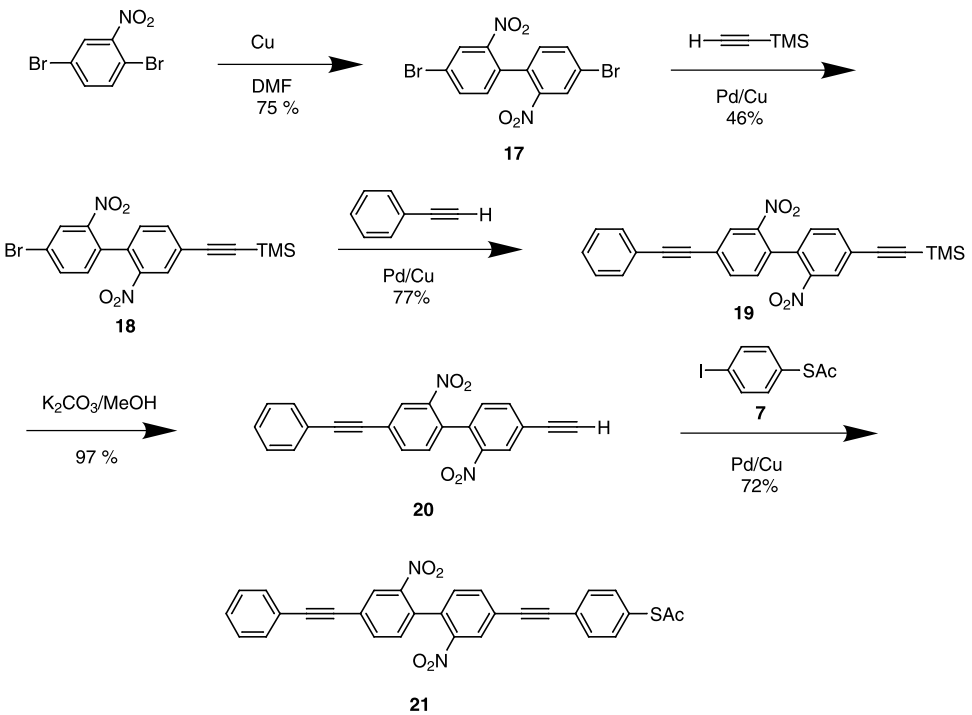


Scheme 4. Synthesis of **16** containing two isonitrile alligator clips.

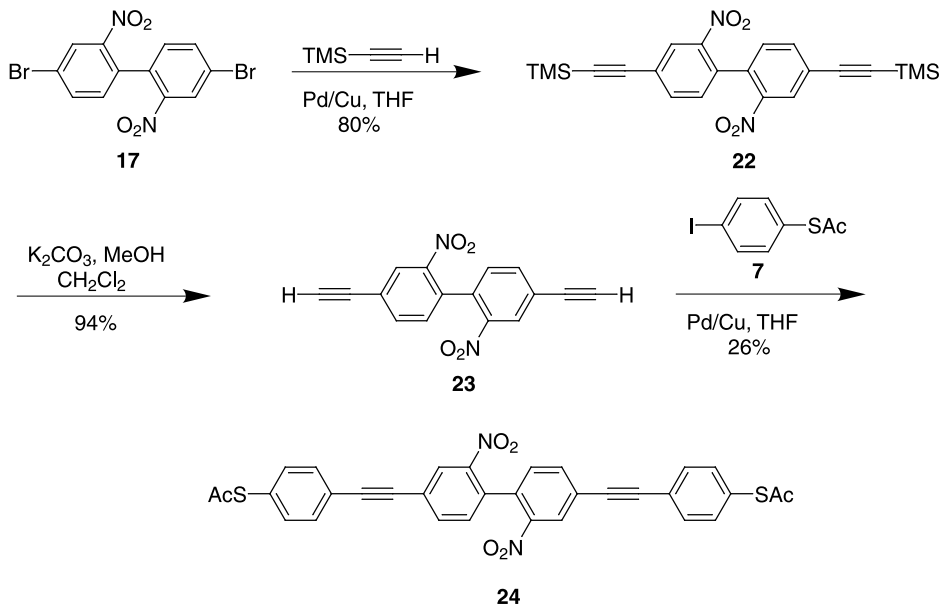
the alkyne.[14] Deprotection of the alkynes provided **13**, which was coupled with 2 equiv. of alligator clip **7** to provide **14** in good yield. No electronic tests have yet been done with this compound. As we have long experienced, the synthesis of the candidate molecules moves far more swiftly than the detailed electrical testing.

Scheme 4 depicts the synthesis of the 2,3′-dinitro device with two isonitrile alligator clips. 4,4′-Diethynyl-2,3′-dinitro-biphenyl (**13**) was coupled with 2 equiv. of formamide **9** to provide **15**. The precise yield could not be ascertained due to the same reasons described earlier. Therefore, crude **15** was taken onto the dehydration step to afford final product **16** in a moderate yield. This is actually an encouraging yield considering the poor solubility of the bis-formamide precursor.

Scheme 5 shows the complete synthesis of another dinitrobiphenyl compound, the 2,2′-isomer. We made this compound since we have yet to determine how regioisomerism affects the electronic characteristics of the molecules. 2,5-Dibromonitrobenzene was subjected to Ullman coupling conditions to give the biphenyl compound **17** in good yield.[16] Coupling of **17** with TMSA afforded **18** in moderate yield. Subsequent coupling with phenylacetylene gave **19**. Deprotection of the alkyne using potassium carbonate and methanol afforded terminal alkyne **20** in high yield. Coupling of **20** with **7** afforded **21** in a surprising 72% yield. This yield is much higher than some other yields of couplings with nitro compounds and thioacetates. It may result from the inability of the nitro group to internally cyclize with the adjacent alkyne, thereby giving fewer by-products.



Scheme 5. Synthesis of regioisomeric 2,2′-dinitrobiphenyl compound **21**.

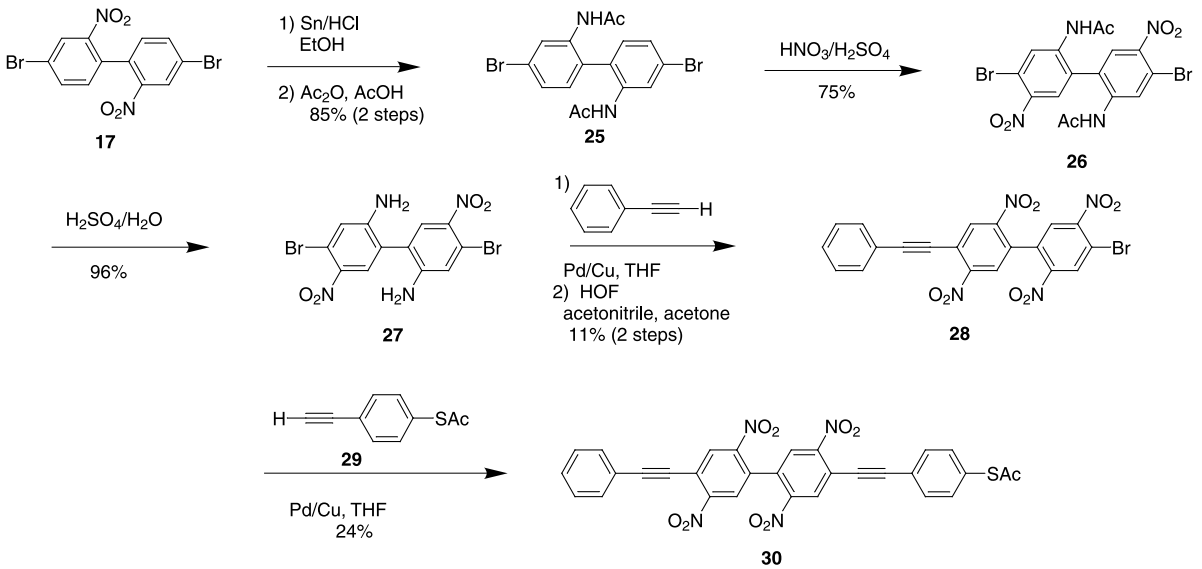


Scheme 6. Synthesis of compounds **24** with two alligator clips.

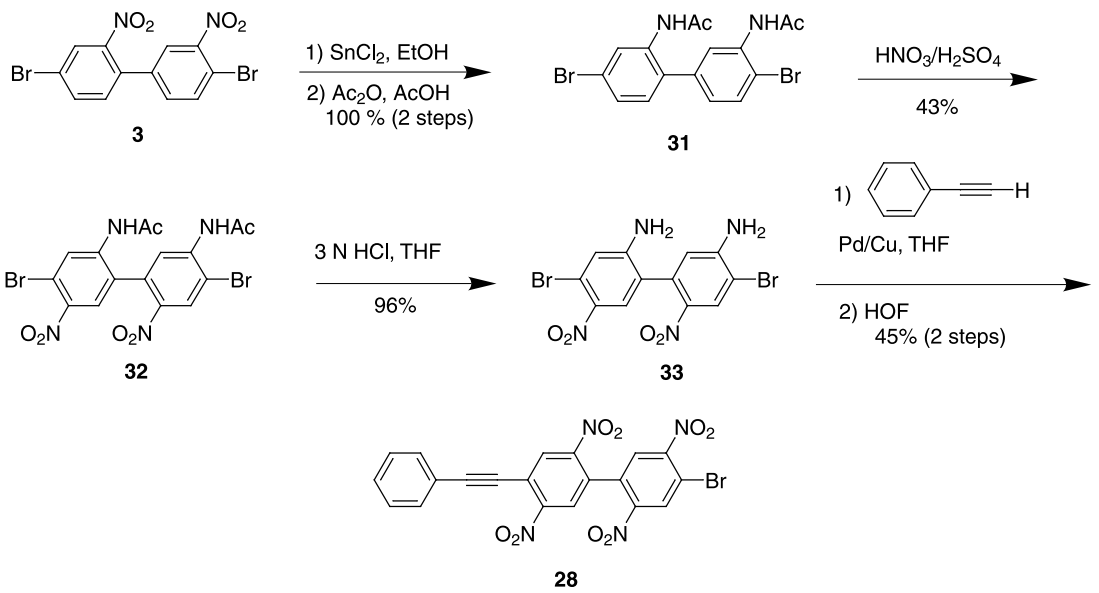
Scheme 6 shows the complete synthesis of the 2,2′-dinitrobiphenyl compound containing two alligator clips for possible use in contacting two metal surfaces or crosslinking nanoparticles. Compound **22** was made by coupling 2 equiv. of TMSA with **17**. Deprotection of the alkynes provided **23**, which was then coupled with 2 equiv. of **7** to provide **24** in low yield.

Scheme 7 shows the complete synthesis of another biphenyl-based candidate. If two nitro groups are good, will a molecule containing four nitro groups have longer lifetime memory states when tested?[3] **17** was reduced to the corresponding diamine. The amines were then protected as acetamides to give **25** in 89% yield over two steps. Mixed acid nitration at 0°C afforded compound **26** in good yield. Potassium carbonate/methanol-promoted deprotection[7] of **26** failed to remove the acetyl groups, but acidic hydrolysis using H_2SO_4 and water easily provided **27**. Coupling of **27** with 1 equiv. of phenylacetylene provided an inseparable mixture of starting material, monocoupled product and dicoupled product, which was taken onto the next step. Hypofluorous acid (HOF, formed from the reaction of F_2 and H_2O) oxidation[17] afforded tetranitro compound **28** in 11% yield over 2 steps. Final coupling of **28** with the alkynyl alligator clip **29**[18] afforded **30** in an expectedly low yield of 24% due to the nitro moieties' proximity to the alkynes. No electrical tests on this compound have yet been conducted.

Scheme 8 shows a synthesis that was designed with the thought that **33** would couple more selectively with phenylacetylene than would **27**, as used in the prior synthesis. Reduction of **3** followed by acetyl protection of the amines afforded **31** in 100% yield over two steps. This yield is higher than that for the previous scheme because some of the 2,2′-dinitrobiphenyl is converted to the

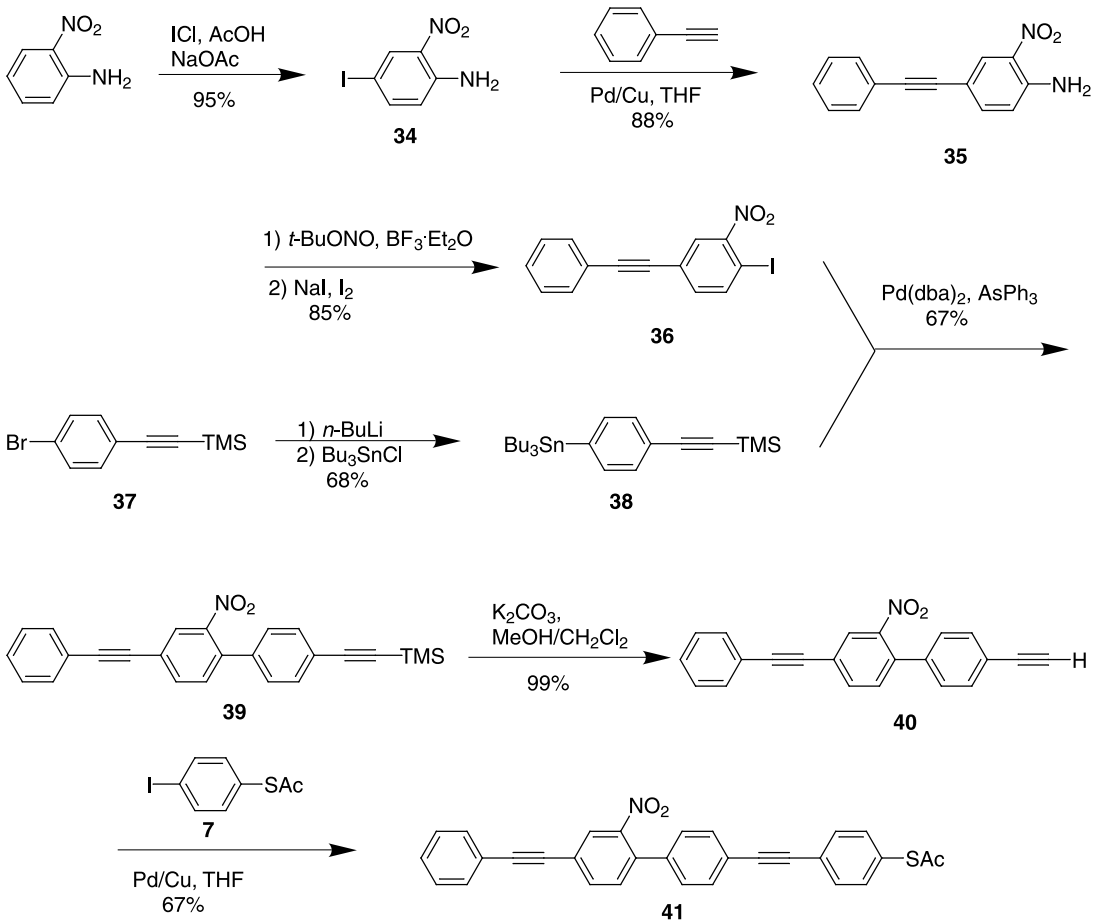


Scheme 7. Synthesis of tetranitro compound **30**.

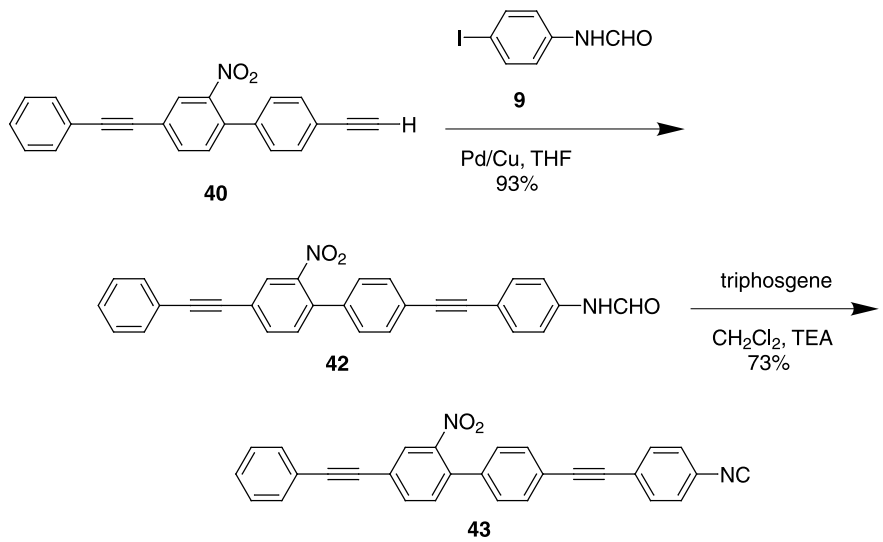


Scheme 8. Improved synthesis of intermediate **28**.

benzo[*c*]cinnoline product instead of the diamine, a conversion that cannot occur for the 2,3′-dinitro isomer. Mixed acid nitration afforded **32** in a modest yield. TLC and proton NMR detected other isomers although they were not isolated. Compound **32** was then deprotected in high yield using 3N HCl in THF to afford **33** with the free amines. The biphenyl core **33** was then coupled with phenylacetylene to give an inseparable mixture of starting material, desired product, and dicoupled material. After some attempt to purify (column chromatography), the mixture was taken onto the oxidation step. The HOF oxidation was used to afford **28** in 45% yield (over two steps).[17] This is an improvement over the prior route that afforded **28** in 11% over two steps from the symmetric biphenyl **27**. Indeed the



Scheme 9. Synthesis of mononitro biphenyl molecule **41**.



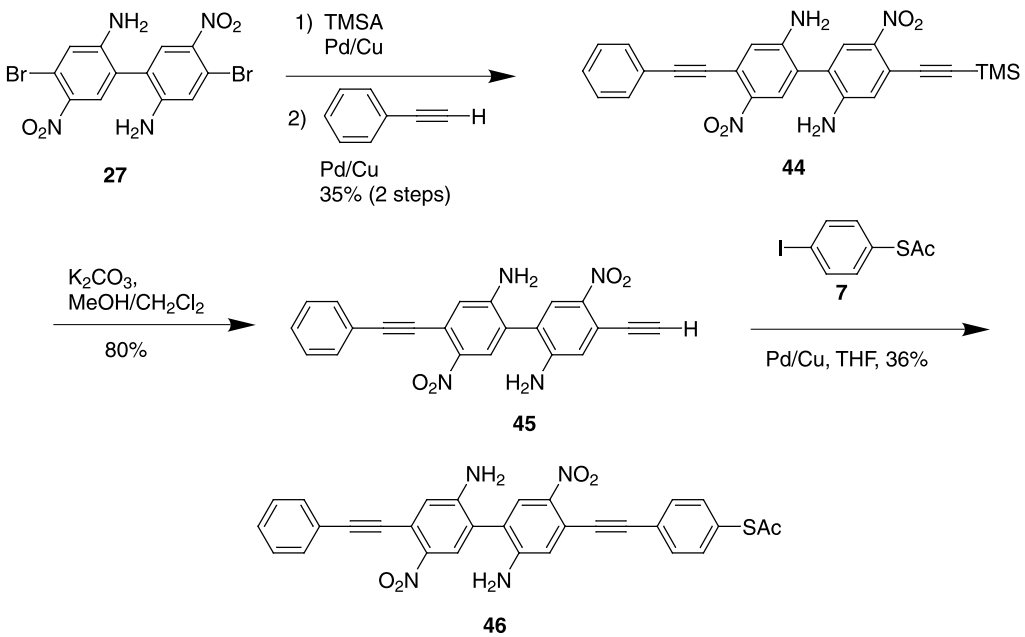
Scheme 10. Synthesis of candidate **43**.

unsymmetrical nature of **33** led to an increase in yield in the Sonogashira coupling.[19]

Scheme 9 shows the complete synthesis of a mononitro biphenyl core-based molecule **41** synthesized to compare its properties to **2** and **14**. The comparison to **2** should reveal any differences produced by adding a barrier (i.e. the biphenyl twist) and length to the molecule. The comparison to **14** should determine what difference exists between having one or two nitro groups on a biphenyl core. The synthesis of **41** began with the iodination of 2-nitroaniline to give **34** in high yield.[20] Coupling of **34** with phenylacetylene provided **35** in high yield. Note that this methodology allows one to generate derivatives of the mononitro device in high yield by coupling of a terminal alkyne at only one available halogen site; a route not easily attainable through other means. Next, the amine was replaced by an iodide via the diazonium salt to give **36**, again in high yield. The production of the second raw material in the parallel synthesis began with the stannylation of **37**[21] to give **38**. This was then subjected to a Stille coupling[22] with **36** to give the biphenyl product **39** in good yield. **39** was deprotected using potassium carbonate and methanol to liberate the terminal alkyne **40** in high yield. **40** was coupled with **7** to give **41** in good yield.

Scheme 10 shows the synthesis of a mononitro biphenyl molecule **43** with an isonitrile alligator clip. 4′-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (**40**) was coupled with formamide **9** to give **42** in high yield. Formamide **42** was then dehydrated using triphosgene to afford isonitrile **43** in a good yield of 73%.

Scheme 11 shows the synthesis of a biphenyl-based device containing two amino groups and two nitro groups. The reasoning behind this design is that if each ring of the



Scheme 11. Synthesis of diamino dinitro biphenyl-based molecule **46**.

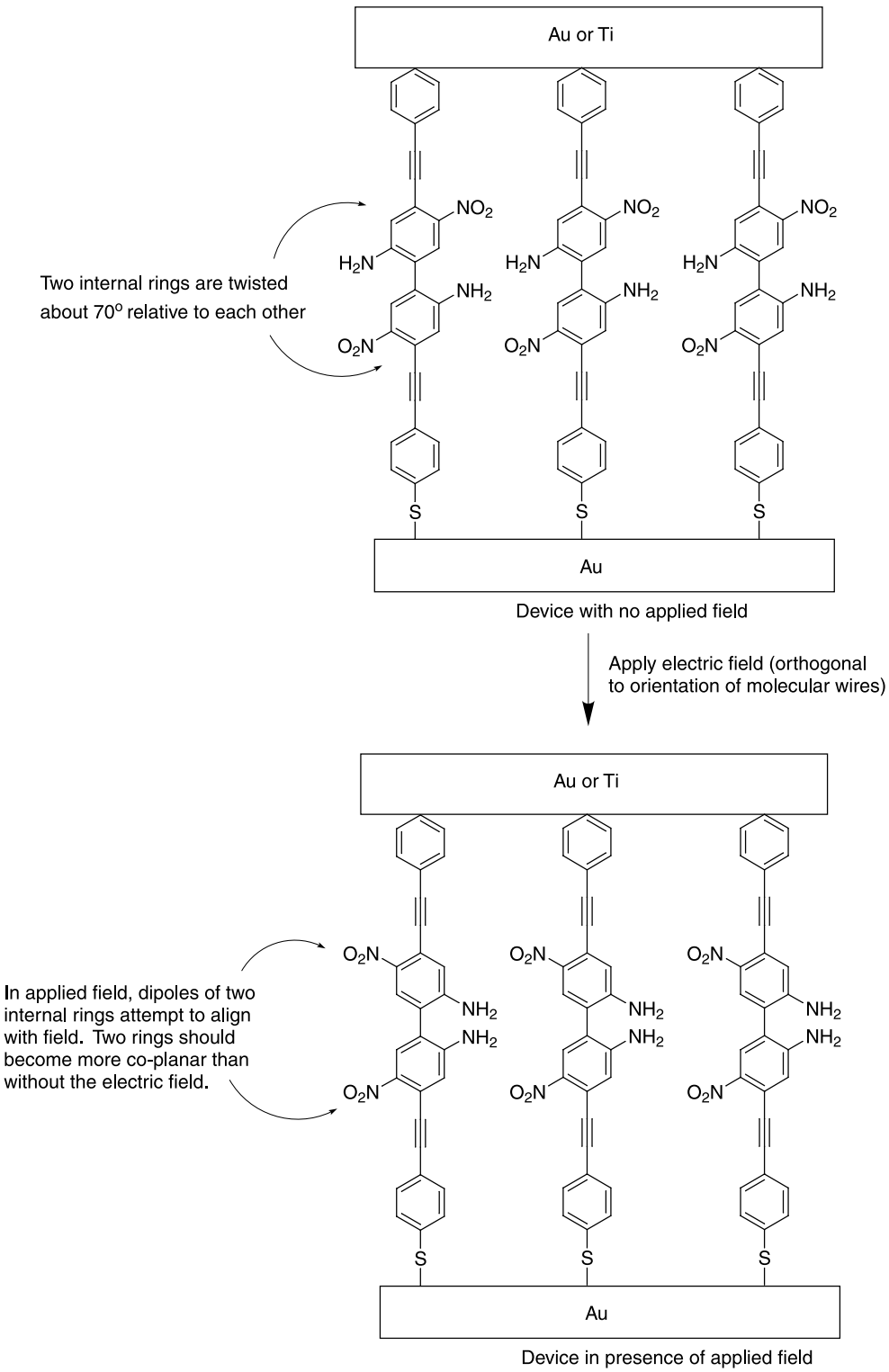
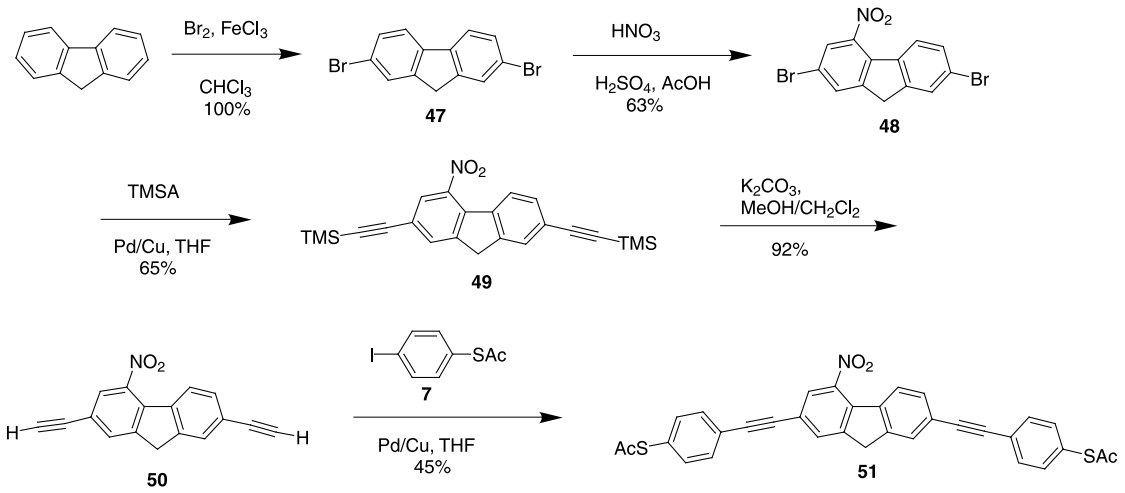


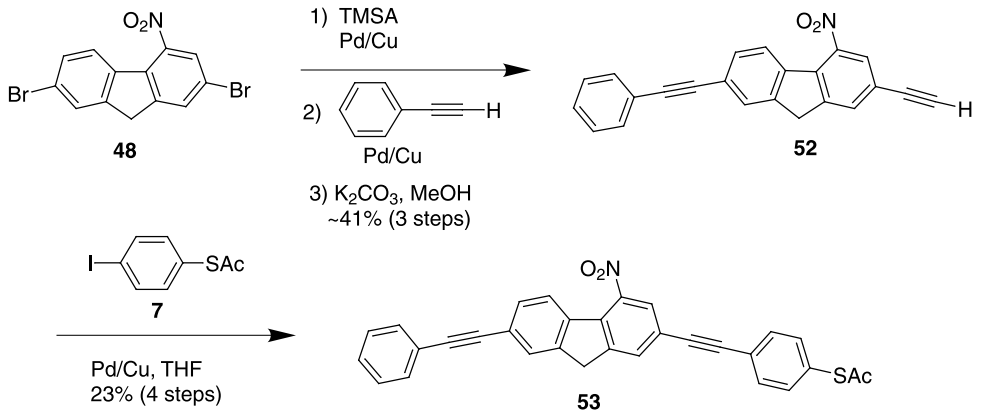
Figure. 2. Schematically depicting the alignment of the internal dipoles and interactions of **46** that may occur in a solid-state device.

biphenyl is in a zwitterionic or pseudo-quinoidal form, the two rings may interact in an interesting manner not seen in any previous devices (Fig. 2). Until some data is generated from the solid-state testing of this compound, it is difficult to speculate on how this system may truly behave.

The synthesis began with compound **27** (Scheme 7). **27** was coupled with 1 equiv. of TMSA to give an intermediate that could not be fully purified via column chromatography. Therefore, after limited purification, the product was coupled with phenylacetylene and purified to give **44** (Scheme 11) in a low, yet statistically expected, yield over the two steps. Deprotection of the terminal alkyne yielded **45**, which was purified by simple filtration through a silica plug. This alkyne was then coupled with **7** to afford **46** in low yield. As we have discussed previously, in our hands the



Scheme 12. Synthesis of fluorene-based molecule **51**.



Scheme 13. Synthesis of fluorene-based molecule **53**.

coupling of nitrated molecules with thioacetyl-containing compounds rarely gives high yields when the nitro moieties are in the 2-position relative to the alkyne.[14]

2.2. Fluorene systems

Scheme 12 shows the first synthesis of a new class of potential molecular electronics devices: fluorene-based compounds. Because the non-planarity of biphenyl cores can create a barrier to conduction (the twist between the rings averages 70°), forcing the rings nearer to planarity by connecting the 2- and 2′-carbons with a methylene bridge, as in fluorene, could lead to molecules with better conduction.

The synthesis began with the bromination of fluorene to give **47** in quantitative yield.[23] Next, **47** was nitrated using mixed acid conditions to give **48**.[24] **48** was coupled with 2 equiv. of TMSA to give **49** in moderate yield. The terminal alkynes were deprotected to give compound **50** in high yield. Finally, the diyne was coupled with 2 equiv. of **7** to afford **51** in a reasonable yield.

Scheme 13 depicts the synthesis of a nitro-fluorene molecule with only one alligator clip. Compound **48** was coupled with TMSA to afford an inseparable mixture of products. After a limited degree of purification, the impure product was coupled with phenylacetylene, again providing an inseparable mixture of products. Deprotection of the terminal alkyne afforded **52** which was >90% pure after column chromatography. The determination of the order of coupling was based on a prior knowledge of Sonogashira couplings.[21] The palladium oxidatively adds to the C–Br bond that is closest and most affected by the electron-withdrawing nitro group. In this case it is the C–Br bond that is in the 3-position relative to the nitro group. Compound **52** was then coupled with **7** to provide final compound **53** in an overall yield of 23% (over 4 steps). The structure of **52** was confirmed via X-ray crystallographic analysis of **53** that provided the ORTEP shown in Figure 3.

Scheme 14 shows the synthesis of **55**, an isomer of **53**, accomplished by simple reversal of the first two coupling steps. Compound **48** was first coupled with phenylacetylene followed by the addition of TMSA in the same reaction

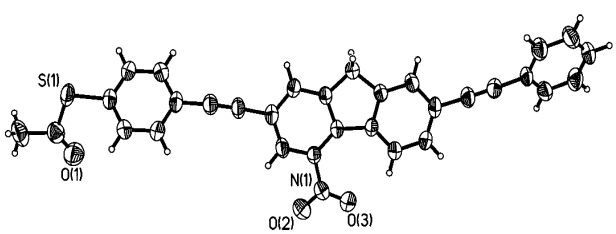
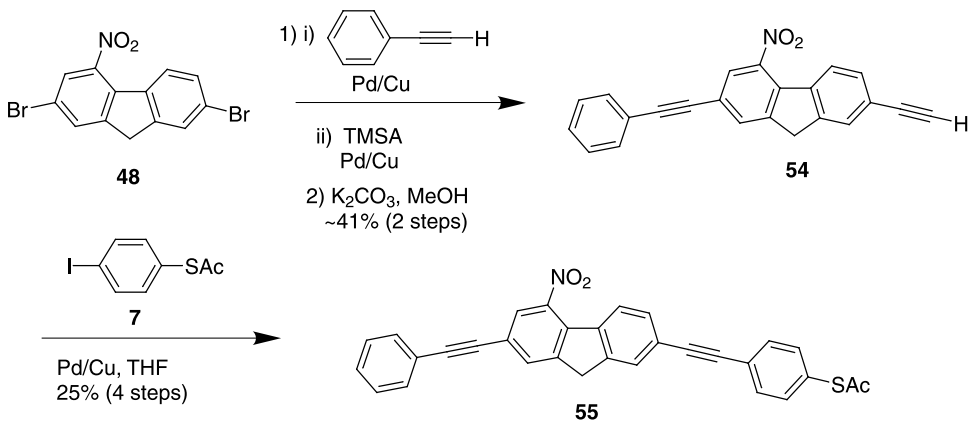
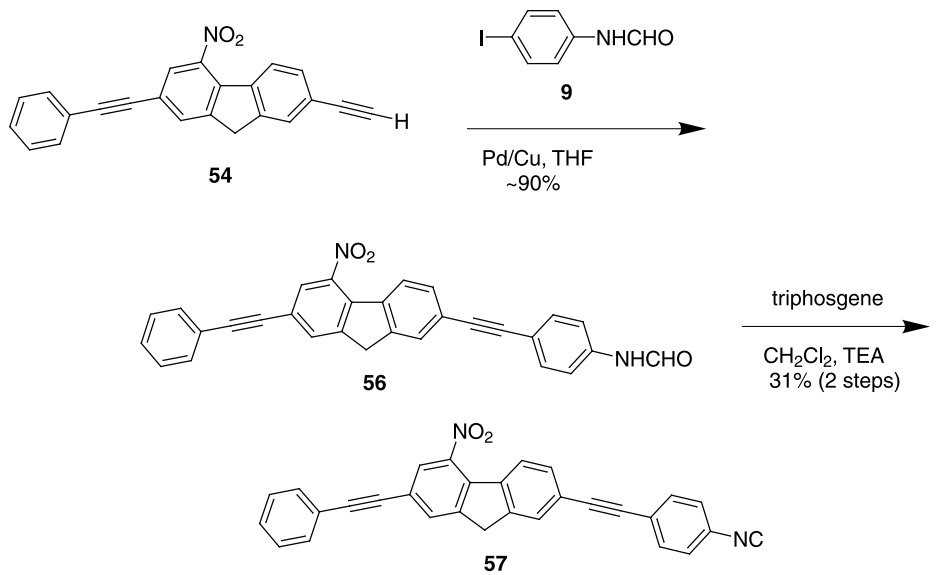


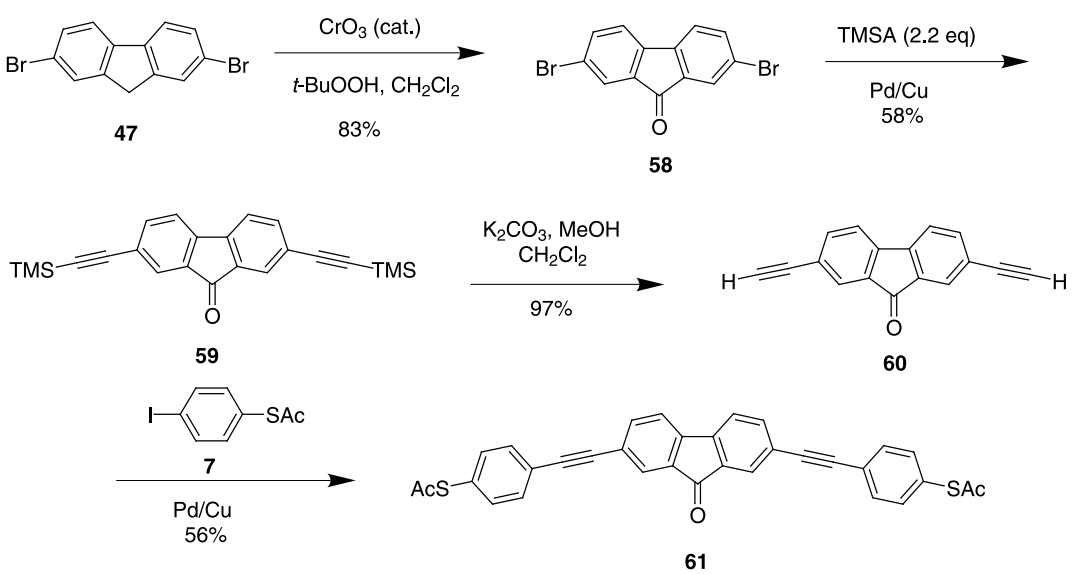
Figure. 3. ORTEP of **53** from X-ray crystallography.



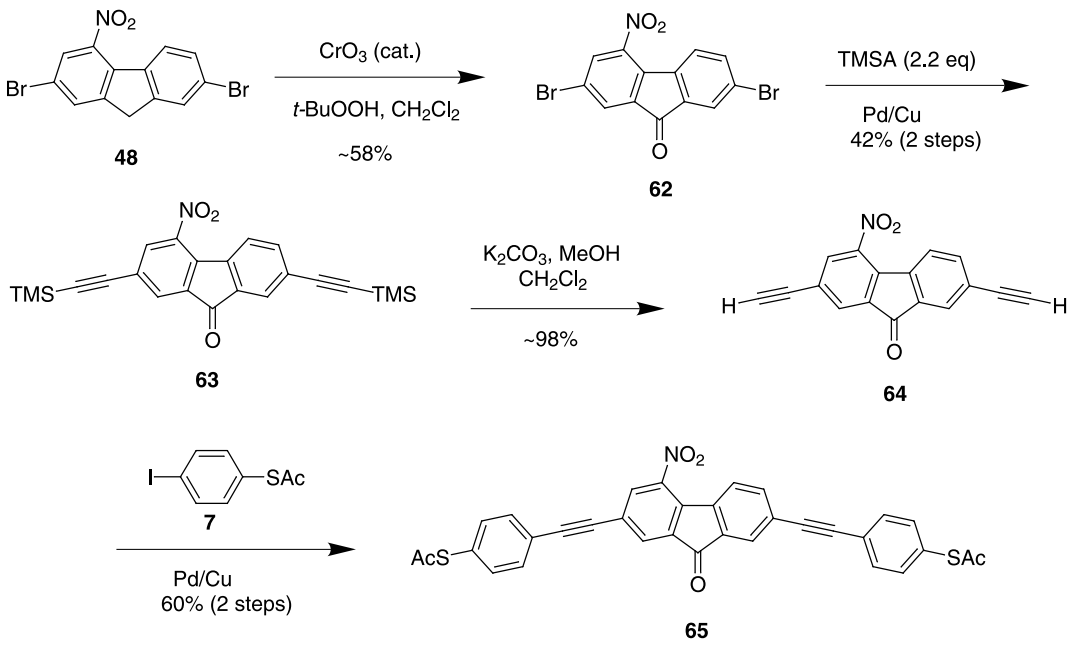
Scheme 14. Synthesis of the isomer of **51**.



Scheme 15. Synthesis of fluorene-based molecule **57** with isonitrile alligator clip.



Scheme 16. Synthesis of fluorenone **61**.



Scheme 17. Synthesis of nitrofluorenone **65** with two alligator clips.

apparatus. Again, this product could not be purified so was taken onto the next step with limited purification. Deprotection of the alkyne afforded **54** in ~38% yield (>90% purity) over the two steps. Coupling of **54** with **7** afforded final compound **55** in 25% yield over the three steps.

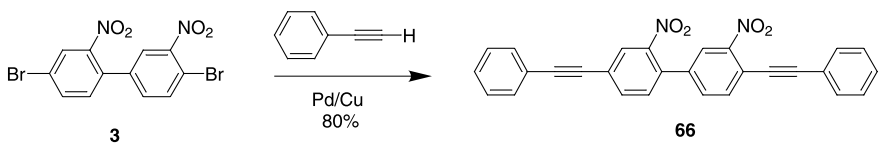
Scheme 15 shows the synthesis of a nitro-fluorene compound containing an isonitrile alligator clip. The synthesis began with the coupling of formamide **9** with 7-ethynyl-4-nitro-2-phenylethynyl-9*H*-fluorene (**54**) to provide **56** in approximately 90% yield (the starting alkyne was not pure). This compound could not be fully purified by column chromatography. Therefore, the slightly impure **56** was dehydrated to give the isonitrile **57** in an overall yield of 31% over two steps.

Scheme 16 shows the synthesis of a molecule containing a fluorenone core. This compound was designed and synthesized based on the concept that the carbonyl functionality of the fluorenone may act as an electron sink and allow for facile reductions. If it demonstrates switching capabilities, **61** would be the first device-like system that we have identified which contains no nitro functionalities. Degradation of the nitro-based devices has been a problem and fluorenones might prove to be more stable. The synthesis began with the oxidation of 2,7-dibromofluorene using a catalytic amount of chromium(VI) oxide and *t*-butyl hydroperoxide to regenerate the catalyst.[25] The reaction proceeded smoothly to afford 2,7-dibromo-9-oxo-fluorene (**58**).[26] Next, **58** was coupled with 2 equiv. of TMSA to afford **59** in unoptimized yield.[27] **59** was deprotected using potassium carbonate and methanol to liberate the free alkynes in high yield.[27] Diyne **60** was coupled with 2 equiv. **7** in a modest yield.

Scheme 17 shows the synthesis of **65** containing a nitrated fluorenone core, combining both nitro and carbonyl functionality. This could provide new and interesting electronic properties in a solid-state device in that there could be two modes of switching and perhaps multiple memory states. The synthesis began with the oxidation of 2,7-dibromo-4-nitrofluorene (**48**) using the catalytic chromium(VI) method described for the previous synthesis[25] but in lower yield, possibly because **48** is more electron-deficient and therefore less susceptible to oxidation.[17] **62** could not be completely purified so it was taken onto the next step, where it was coupled with 2 equiv. of TMSA to afford **63** in a modest yield over the two steps. **63** was then deprotected to afford **64** in high yield. The liberated alkynes were then coupled with 2 equiv. of **7** to afford **65** in a good yield.

3. Cyclic voltammetry results

We have used cyclic voltammetry (CV) to help us understand how some of our molecules might behave as switches and memory elements.[10] We used the same CV testing methods on the new products in order to predict how these nanoscale structures may behave in a solid-state device. We concede that the comparisions would only be qualitative since the electrochemical (solvent-based with electrolyte) and solid-state (solvent-free, no electrolyte) are dramatically different.



Scheme 18. Synthesis of compound **66** with no alligator clips.

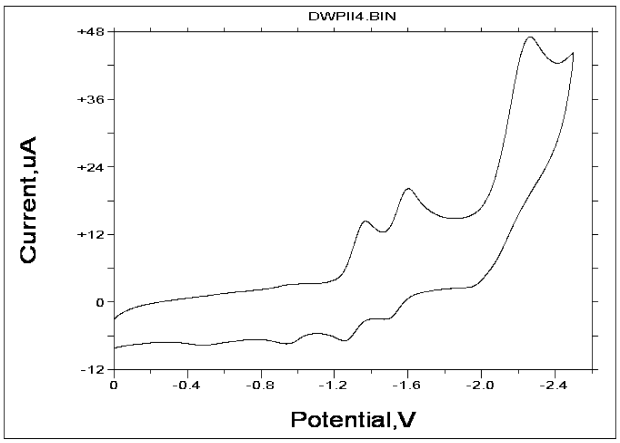
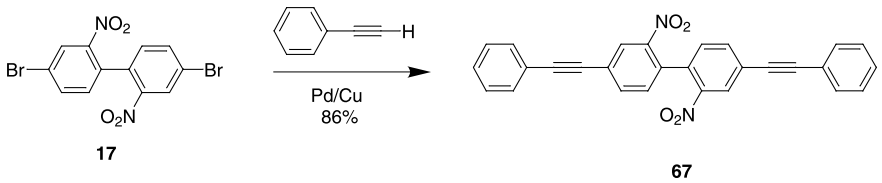


Figure. 4. CV of **66**. The reduction potentials were found to be −1.37, −1.60, and −2.26 V.



17 **67**

Scheme 19. Synthesis of **67** for CV studies.

Scheme 18 shows the synthesis of the 2,3′-dinitrobiphenyl compound **66** with no alligator clips, similar to **8**, but without the S–Ac. It is beneficial to study similar compounds that differ only by the presence or absence of the S–Ac group since hydrolysis of the acetate under conditions of the CV testing could skew the results. **66** was therefore synthesized for the sole purpose of our electrochemical testing. **3** was coupled with an excess of phenylacetylene to afford compound **66** in a yield of 80%. The CV for this compound is shown in Figure 4. There are three distinct reduction peaks, although they are only quasi-reversible. The first and third potentials are approximately the same as the first and second potentials of **2** studied previously.[10] Interestingly, **66** has a third reduction not seen in any of the previous devices. It is reasonable that the new reduction is due to the presence of the second nitro group. This new reduction potential is −1.60 V, which is approximately 0.2 V difference from the first potential. From this data **66** should have better electronic properties than previous systems, and this is precisely what has been observed. From preliminary solid-state testing of **8**, the switching ON potential of the 2,3′-dinitro biphenyl device is approximately 2.7 V and the switching 'OFF' potential is approximately 2.9 V.[28,25] The difference between these ON–OFF voltages is approximately 0.2 V, closely corresponding to the difference in the first two CV reduction potentials.

Our working theory of how these molecules behave as switches is based on the idea that the molecules in the solid state get reduced as the voltage is increased and the reduction is concomitant with a conformational change. This gives rise to the switching ON of the device because of changes to the molecular orbitals of the molecule and delocalization of the charge over the entire molecule as molecular orbitals overlap, producing conduction. As the potental becomes higher, the molecules get reduced a second time thereby changing the electronic properties again. This leads to the switching OFF of the device putting it in a lower conductivity state.[10] The CV data lends more support to this proposed theory of switching operation.

Scheme 19 shows the synthesis of the 2,2′-dinitro-biphenyl compound **67** with no alligator clips for further CV experiments. **17** was coupled with an excess of phenylacetylene to afford compound **67** in good yield. CV measurements were performed and can be seen in Figure 5. The quasi-reversible reduction potentials are almost identical to the first two reductions of **66**. However, there is no third reduction at −2.0 to −2.2 V, as was seen with **66**. One could reason that the third reduction of **66** leads to a reaction between the 3′-nitro group and the 4′-alkyne of **66**. This is reasonable because nitro groups and alkynes are known to react in an intramolecular fashion to form isatogens.[14] The 2,2′-dinitro compound **67** does not have such a 3′-nitro-4′-alkyne relationship and therefore cannot form isatogen side-products.

Figure 6 shows results from the CV testing of tetranitro compound **30**. The two voltammagrams **6a** and **6b** represent the same compound from different synthetic batches. As can be seen, the CVs look similar but are not exactly the same. This could be because the tetra-nitro device is very redox reactive and is not stable. Upon close examination, there appear to be several reductions in both CVs between −0.7 V and −1.4 V. Since there are four nitro groups located in this system, several reductions may overlap, thereby making the voltammagrams difficult to interpret. Based on this analysis,

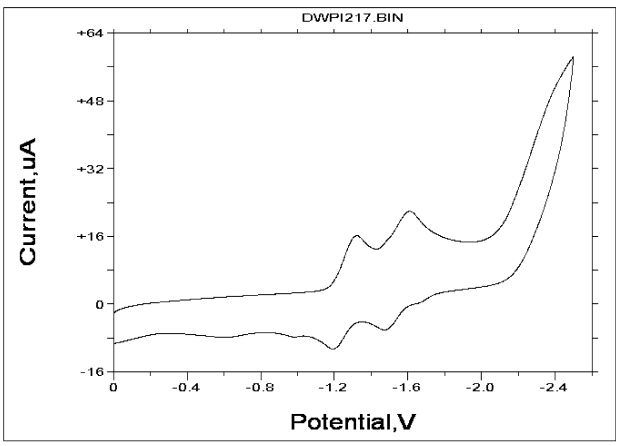
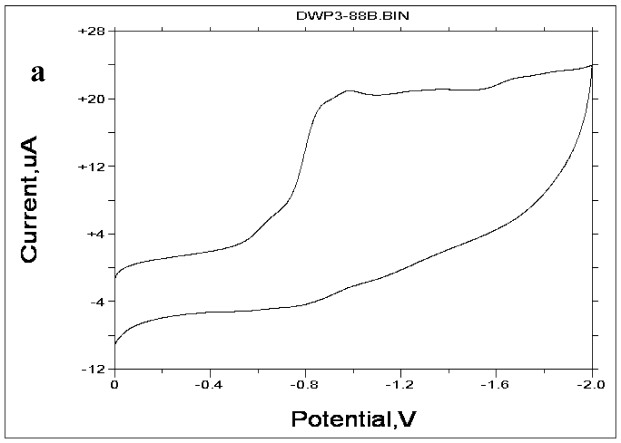


Figure. 5. CV of **67**. The reduction potentials were found to be −1.32, 1.61 V.



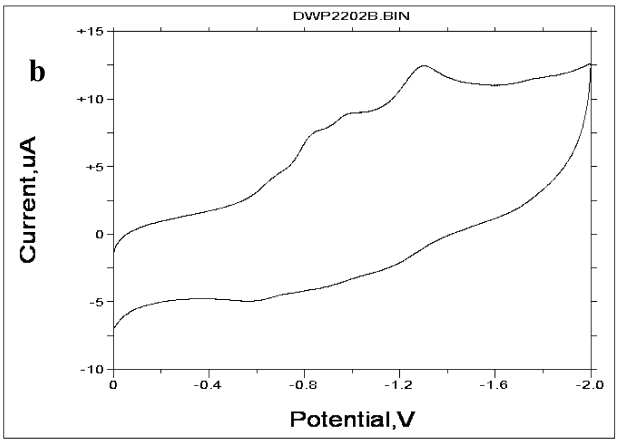


Figure. 6. CVs (a) and (b) of different batches of tetranitro compound **30**.

this device may be an excellent redox center for use in our molecular electronics studies; however, its lack of stability may be a problem.

Figure 7 shows the CV results of the mononitro biphenyl device **41**. As can be seen in the plot, there are again two reductions, one at −1.47 V and another at −2.19 V. These potentials are close to those of **2**, however, the second reduction here is much less pronounced than that for **2**. As was seen with the 2,2′-dinitro biphenyl device **67**, there is no spatially close relationship between a 3′-nitro group and a

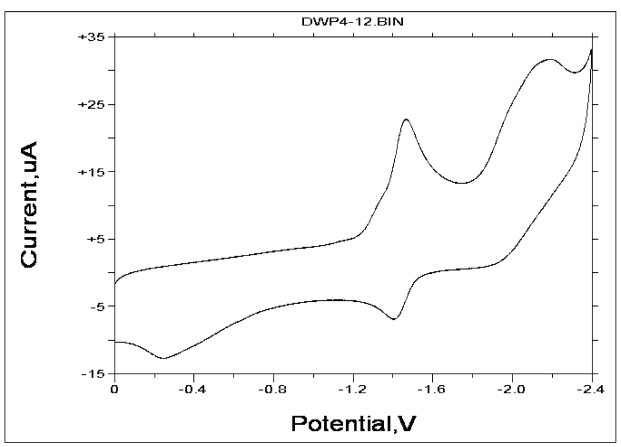


Figure. 7. CV of mononitro biphenyl molecule **41**.

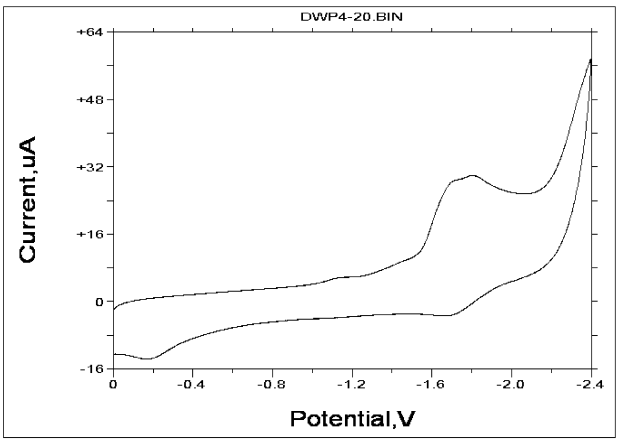


Figure. 8. CV of dinitro–diamino molecule **46**.

4′-alkyne in compound **41**. Because there is no possibility of an intramolecular cyclization reaction between those groups, the second reduction might be rather weak because it is due to an intermolecular coupling.

The CV for dinitro-diamino device **46** is shown in Figure 8. Although this compound was not designed to rely on its redox properties to behave as a functional device (it should rely on the ability of dipole moments of the internal rings to align with an applied electric field as shown in Fig. 2), the electrochemical properties were measured to compare with the other devices. Two reductions are present, in what appears to be overlapping peaks. It is estimated that there are two reductions at −1.71 V and −1.80 V, probably due to the presence of two nitro groups on the system.

Figure 9 shows the CV of nitro-fluorene compound **55**. There is a clearly visible reduction peak at −1.40 V and another reduction, which is not so clear, at −2.0 V. These are similar to the results for the mono-nitro biphenyl compound **41** which showed reductions at −1.47 V and −2.19 V. The second reduction of the **41** was likewise not well-defined. These compounds have very similar CVs with only a minor shift in reduction potentials.

Figure 10 shows the CV for fluorenone compound **61**. The graph shows a single reduction at −1.45 V that appears to

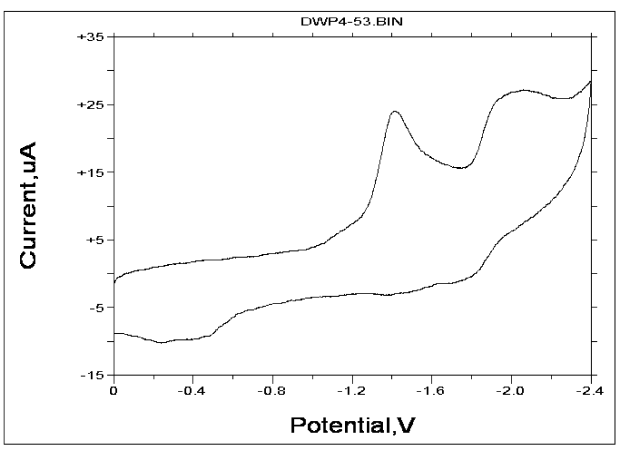


Figure. 9. CV for compound **55**.

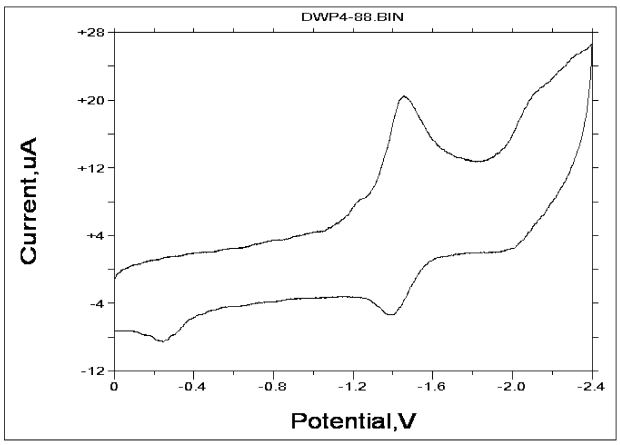


Figure. 10. CV of fluorenone molecule **61**.

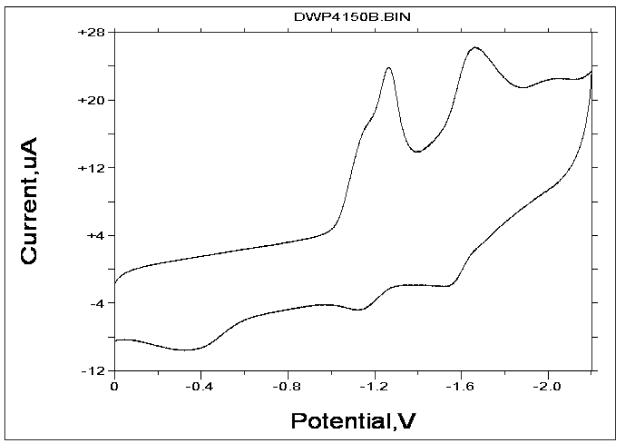


Figure. 11. CV of compound **65**.

be quasi-reversible. This is almost the same value for the reduction potential for the nitro-fluorene **55**. One could argue that there is a second reduction at −2.1 V but it is not clear. This data suggests that this device may give similar results to previously tested compounds when tested in a solid-state testbed such as the nanopore device.

The CV for the nitro-fluorenone molecule **65** is shown in Figure 11. This compound shows two obvious reduction peaks. The reduction potentials are −1.26 V and −1.66 V. Other than the tetra-nitro device, the first reduction is the lowest reduction potential observed for any biphenyl or fluorenyl-based compound. It appears that the first reduction peak may be two close, overlapping peaks, with the first reduction being approximately −1.16 V.

We made minimal effort to exclude air in any of our CV work, therefore repeatability was generally poor, especially with the products containing the S−Ac group.

4. Conclusions

Many different molecular electronics device candidates have been synthesized with a few tested to date in full device embodiments. These device candidates were rationally designed based on chemical intuition using the solid-state results we have received from collaborators. Although absolute values of the reduction potentials cannot be compared between the nanopore (pseudo-solid state) and solution experiments, solution CV helps to support the proposed mechanism wherein reduction of the system occurs to open or close a transport channel. Also, it is hoped that CV testing may prove to be a method of quick-screening compounds prior to solid-state testing as well as a way to predict solid-state electronic properties. However, more data needs to be obtained before this can be firmly established.

5. Experimental

5.1. General

All reactions were performed under an atmosphere of nitrogen unless stated otherwise. *N*,*N*-dimethylformamide (DMF) was distilled over calcium hydride and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexanes were distilled. *N*,*N*-Diisopropylethylamine (DIEA) was distilled over calcium hydride. Silica gel plates were 250 μm thick, 40 F_{254} grade from EM Science. Silica gel was grade 60 (230–400 mesh) from EM Science. ^{1}H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Melting points were determined on a Büchi melting point apparatus. Mass spectrometry was performed at Rice University's mass spectrometry lab. All new compounds were named using the Beilstein AutoNom feature of Beilstein Commander software. The synthesis of compound **7** was described previously[29] as was the synthesis of compound **9**.[30]

5.2. General procedure for the coupling of a terminal alkyne with an aryl halide utilizing a palladium–copper cross-coupling (Castro–Stephens/Sonogashira Protocol)[19,31]

To an oven-dried screw cap tube or a round bottom flask equipped with a water cooled West condenser and a magnetic stir bar 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). Alternately, bis(dibenzylideneacetone)palladium(0) (2 mol% based on aryl halide), copper(I) iodide (2 mol% based on aryl halide) and triphenylphosphine (2.5 equiv. per palladium) were used. The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). A co-solvent system of THF was added followed by DIEA. The terminal alkyne was then added and the reaction heated, if necessary, until complete. The reaction vessel was cooled to room temperature and the mixture quenched with water or a saturated solution of NH_4Cl. The organic layer was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3×). The combined aqueous layers were extracted with CH_2Cl_2 (3×). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).

5.3. General procedure for the deprotection of a trimethylsilyl (TMS) protected alkyne

To a round bottom flask equipped with a magnetic stir bar were added the TMS-protected alkyne, 4–6 equiv. of potassium carbonate, and a 1:1 mixture of methanol and CH_2Cl_2. The reaction vessel was sealed with a rubber septum and then filled with nitrogen. The reaction was allowed to go to completion at which time the reaction was quenched with a saturated solution of NaCl. The resulting solution was extracted as stated in the previous section with the resulting terminal alkyne quickly employed in the next palladium/copper cross-coupling step.

5.4. General procedure for electrochemical testing of potential moletronics devices

The CVs were performed on a BAS CV-50W using a glassy carbon electrode as working electrode, platinum wire as auxiliary electrode, with a $Ag/AgNO_3$ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1 M *n*-Bu_4NBF_4. The scan rate was 0.1 V/s at 25°C.

5.4.1. 4,4′-Dibromo-2,3′-dinitro-biphenyl (3).[13] Nitric acid (70%, 30.6 mL) was added to a 100 mL round bottom flask containing a stir bar and cooled to approximately 0°C in an ice bath. 4,4′-Dibromobiphenyl (4.01 g, 12.8 mmol) was then slowly added to the acid and stirred at 0°C for 40 min. Ice water was then added to the mixture at which point a light yellow solid precipitated out of the solution. The solid was filtered and washed with water then air-dried. Recrystallization from ethanol/acetone afforded the desired product as yellow needles (3.59 g, 70% yield): mp 150–151°C (lit. mp 152–153°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=2.0 Hz, 1H), 7.82 (dd, J=8.3, 2.0 Hz, 1H), 7.79 (d, J=0.4 Hz, 1H), 7.78 (d, J=6.8 Hz, 1H), 7.30 (dd, J=8.2, 2.2 Hz, 1H), 7.29 (d, J=8.1 Hz, 1H).

5.4.2. (4′-Bromo-3,2′-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (4). 4,4′-Dibromo-2,3′-dinitrobiphenyl (**3**) (1.00 g, 2.49 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.088 g, 0.125 mmol), copper(I) iodide (0.047 g, 0.249 mmol), THF (10 mL), DIEA (1.73 mL, 9.96 mmol), and TMSA (0.39 mL, 2.7 mmol) were used for 4 h at RT following the general procedure for couplings. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product as a brown solid (0.605 g, 58% yield): mp 106–108°C. IR (KBr) 3098.7, 3068.3, 2955.3, 2852.9, 2069.4, 1597.9, 1525.5, 1462.9, 1347.1, 1250.9, 1152.4, 1099.1, 1036.9, 866.9, 840.2, 826.6, 760.3, 536.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=1.8 Hz, 1H), 7.93 (d, J=1.8 Hz, 1H), 7.80 (dd, J=8.1, 1.9 Hz, 1H), 7.66 (d, J=7.9 Hz, 1H), 7.42 (dd, J=8.0, 1.8 Hz, 1H), 7.30 (d, J=8.3 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.0, 138.0, 136.6, 135.8, 133.5, 132.9, 132.5, 128.2, 124.4, 123.5, 118.9, 106.0, 99.3, 0.0. HRMS calcd for $C_{17}H_{15}N_2O_4BrSi$: 419.9967. Found: 419.9963 (Error=0.9 ppm).

5.4.3. (3,2′-Dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (5). (4′-Bromo-3,2′-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (**4**) (0.509 g, 1.21 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.043 g, 0.061 mmol), copper(I) iodide (0.023 g, 0.121 mmol), triphenylphosphine (0.032 g, 0.121 mmol), THF (20 mL), DIEA (0.84 mL, 4.84 mmol), and phenylacetylene (0.20 mL, 1.82 mmol) were used following the general procedure for couplings. The tube was capped and the solution was heated in a 70°C oil bath for 1 d. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product as brown oil (0.355 g, 67% yield). IR (KBr) 3065.8, 2958.3, 2883.6, 2213.7, 2160.5, 1530.7, 1490.9, 1347.7, 1249.5, 1078.8, 891.0, 844.6, 756.4, 689.6, 527.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=1.6 Hz, 1H), 8.00 (d, J=1.8 Hz, 1H), 7.78 (dd, J=8.0, 1.6 Hz, 1H), 7.68 (d, J=8.0 Hz, 1H), 7.55 (m, 2H), 7.45 (dd, J=8.0, 1.8 Hz, 1H), 7.39 (m, 4H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.8, 138.5, 135.9, 135.7, 133.2, 132.5, 132.3, 132.2, 129.7, 129.0, 128.0, 125.9, 124.5, 122.3, 118.8, 105.9, 99.4, 93.8, 86.4, 0.0. HRMS calcd for $C_{25}H_{20}N_2O_4Si$: 440.1192. Found: 440.1187 (Error=1.2 ppm).

5.4.4. 4′-Ethynyl-2,3′-dinitro-4-phenylethynyl-biphenyl (6). (3,2′-Dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (**5**) (0.334 g, 0.758 mmol), potassium carbonate (0.524 g, 3.79 mmol), methanol (20 mL), and CH_2Cl_2 (20 mL) were used following the general procedure for deprotection to afford the desired product as brown oil (0.274 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=1.5 Hz, 1H), 8.02 (d, J=1.7 Hz, 1H), 7.78 (dd, J=8.0, 1.6 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.55 (m, 2H), 7.48 (dd, J=8.0, 1.8 Hz, 1H), 7.38 (m, 4H), 3.58 (s, 1H).

5.4.5. Thioacetic acid *S*-[4-(3,2′-dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl] ester (8). 4′-Ethynyl-2,3′-dinitro-4-phenylethynyl-biphenyl (**6**) (1.10 g, 2.99 mmol)) was coupled with 4-thioacetyl-1-iodobenzene (**7**)[26] (0.831 g, 2.99 mmol) using the Pd/Cu cross coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.086 g, 0.149 mmol), copper(I) iodide (0.057 g, 0.30 mmol), triphenylphosphine (0.157 g, 0.60 mmol), THF (20 mL), and DIEA (2.1 mL, 12.0 mmol) in a screw cap tube under nitrogen. The solution was stirred in a 50°C oil bath for 3 h. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.70) afforded the desired product as an orange solid (0.981 g, 63% yield): mp 156–158°C. IR (KBr) 3078.2, 2924.6, 2858.0, 2207.6, 1709.0, 1528.4, 1495.7, 1346.2, 1280.9, 1112.6, 846.6, 827.0, 760.8, 691.0, 618.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J=1.6 Hz, 1H), 8.09 (d, J=1.9 Hz, 1H), 7.79 (dd, J=8.0, 1.7 Hz, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.62 (dt, J=8.2, 1.8 Hz, 2H), 7.56 (m, 2H), 7.51 (dd, J=8.1, 1.8 Hz, 1H), 7.43 (m, 3H), 7.38 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 150.0, 148.8, 138.5, 136.0, 135.3, 134.7, 133.2, 133.0, 132.7, 132.3, 132.3, 130.0, 129.7, 129.0, 128.0, 126.0, 124.8, 123.8, 122.4, 118.4, 98.0, 93.8, 86.7, 86.4, 30.8. HRMS calcd for $C_{30}H_{18}N_2O_5S$: 518.0936. Found: 518.0947 (Error=2.0 ppm).

5.4.6. *N*-[4-(3,2′-Dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide (10). 4′-Ethynyl-3,2′-dinitro-4-phenylethynyl-biphenyl (**6**) (1.10 g, 2.99 mmol) was coupled with *N*-(4-iodo-phenyl)-formamide (**9**)[27] (0.739 g, 2.99 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.086 g, 0.150 mmol), copper(I) iodide (0.057 g, 0.300 mmol),

triphenylphosphine (0.157 g, 0.600 mmol), DIEA (2.1 mL, 12 mmol), and THF (20 mL). After stirring at 55°C for 4 h, the reaction mixture was washed with NH_4Cl (aq) and CH_2Cl_2. The resulting solution was diluted with hexanes to precipitate the desired compound (1.48 g) that was taken onto the next step with no further purification. IR (KBr) 3361.9, 3073.1, 2202.5, 1692.6, 1600.5, 1520.1, 1405.4, 1337.3, 1282.2, 1238.6, 1144.5, 834.0, 753.7, 685.6 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 8.43 (s, 0.73H), 8.26 (d, J=1.7 Hz, 1H), 8.22 (d, J=1.6 Hz, 1H), 8.00 (dd, J=8.1, 1.7 Hz, 1H), 7.94 (d, J=8.1 Hz, 1H), 7.82–7.76 (m, 4.1H), 7.67–7.60 (m, 4.63H), 7.49 (m, 3.43H).

5.4.7. 4′-(4-Isocyano-phenylethynyl)-2,3′-dinitro-4-phenylethynyl-biphenyl (11). To a large test tube was added *N*-[4-(3,2′-dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide (**10**) (0.500 g, 1.03 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (40 mL) and triethylamine (10 mL) was added and the solution was cooled to 0°C. Triphosgene (0.278 g, 1.03 mmol) was then added. After 2 h starting material remained by TLC. An additional 0.139 g (0.51 mmol) of triphosgene was added. After 45 min, an additional 0.139 g (0.51 mmol) of triphosgene was added. After 15 additional min, 0.278 g (1.03 mmol) of triphosgene was added (total of 3 equiv.). After 4.5 h (total time), the reaction was complete by TLC. The mixture was washed with NaCl (aq) and CH_2Cl_2. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) afforded the product as a yellow solid (0.438 g, 91% yield): mp 160°C (decomp.). IR (KBr) 2119.7, 1525.6, 1341.3, 840.4, 761.6, 691.6, 543.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=1.4 Hz, 1H), 8.10 (d, J=1.6 Hz, 1H), 7.80 (dd, J=8.0, 1.3 Hz, 1H), 7.75 (d, J=8.1 Hz, 1H), 7.62 (d, J=8.3 Hz, 2H), 7.57–7.52 (m, 3H), 7.43 (d, J=7.9 Hz, 1H), 7.40–7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 150.0, 148.8, 138.9, 136.0, 135.2, 133.5, 133.1, 132.8, 132.3, 132.2, 129.8, 129.0, 128.0, 127.2, 127.0, 126.1, 124.9, 124.1, 122.3, 118.4, 96.7, 93.9, 87.4, 86.7. HRMS calcd for $C_{29}H_{15}N_3O_3$: 469.106256. Found: 469.107078 (Error=1.8 ppm).

5.4.8. 2,3′-Dinitro-4,4′-bis-trimethylsilanylethynyl-biphenyl (12). 4,4′-Dibromo-2,3′-dinitro-biphenyl[13] (**3**) (1.50 g, 3.73 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.131 g, 0.187 mmol), copper(I) iodide (0.071 g, 0.373 mmol), THF (20 mL), DIEA (5.2 mL, 30 mmol) and TMSA (1.32 mL, 9.33 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 17 h. Flash column chromatography (silica gel using 1:1 CH_2Cl_2/hexanes as eluent; R_f=0.59) afforded the desired product (1.20 g, 74% yield): mp 82–90°C. IR (KBr) 3073.1, 2960.4, 2899.2, 2164.0, 1533.8, 1477.8, 1348.8, 1250.8, 1219.9, 1079.1, 847.5, 760.3, 643.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=1.6 Hz, 1H), 8.00 (d, J=1.8 Hz, 1H), 7.74 (dd, J=8.0, 1.6 Hz, 1H), 7.70 (d, J=8.0 Hz, 1H), 7.46 (dd, J=8.0, 1.9 Hz, 1H), 7.39 (d, J=7.9 Hz, 1H), 0.31 (s, 9H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.6, 138.4, 136.3, 135.7, 133.5, 132.4, 132.1, 128.4, 125.7, 124.5, 118.8, 105.9, 101.8, 99.7, 99.3, 0.1, −0.01. HRMS calcd for $C_{22}H_{24}N_2O_4Si_2$: 436.127465. Found: 436.126508. (Error=2.2 ppm).

5.4.9. 4,4′-Diethynyl-2,3′-dinitro-biphenyl (13). 2,3′-Dinitro-4,4′-bis-trimethylsilanylethynyl-biphenyl (12). (0.815 g, 1.87 mmol), potassium carbonate (1.55 g, 11.2 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were used following the general procedure for deprotection to afford the desired product (0.508 g, 93% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=1.3 Hz, 1H), 8.06 (d, J=1.7 Hz, 1H), 7.79 (m, 2H), 7.51 (dd, J=7.9, 1.7 Hz, 1H), 7.44 (d, J=8.0 Hz, 1H), 3.63 (s, 1H), 3.33 (s, 1H).

5.4.10. Thioacetic acid *S*-{4-[4′-(4-acetylsulfanyl-phenylethynyl)-3,2′-dinitro-biphenyl-4-ylethynyl]-phenyl} ester (14). 4,4′-Diethynyl-2,3′-dinitro-biphenyl (**13**) (1.26 g, 4.31 mmol), bis(dibenzylideneacetone)palladium(0) (0.124 g, 0.216 mmol), copper(I) iodide (0.082 g, 0.431 mmol), triphenylphosphine (0.226 g, 0.862 mmol), THF (20 mL), DIEA (4.5 mL, 25.9 mmol), and 4-(thioacetyl)iodobenzene (**7**)[29] (2.40 g, 8.62 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at 55°C for 4.5 h. Flash column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.45) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as a slightly yellow solid (1.52 g, 59% yield): mp 176–179°C (decomp.). IR (KBr) 3073.1, 2211.7, 1709.3, 1534.1, 1348.8, 1118.5, 951.2, 827.0, 623.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=1.7 Hz, 1H), 8.11 (d, J=1.8 Hz, 1H), 7.82 (dd, J=8.0, 1.6 Hz, 1H), 7.77 (d, J=8.1 Hz, 1H), 7.64 (dt, J=8.2, 1.7 Hz, 2H), 7.59 (dt, J=8.2, 1.7 Hz, 2H), 7.53 (dd, J=8.0, 1.8 Hz, 1H), 7.45 (m, 5H), 2.452 (s, 3H), 2.446 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 150.0, 148.8, 138.4, 136.1, 135.3, 134.8, 134.7, 133.5, 133.0, 132.8, 132.7, 132.3, 130.0, 129.9, 128.1, 125.6, 124.8, 123.8, 123.5, 118.9, 98.0, 92.9, 88.2, 86.4, 30.8. MALDI-MS calcd for $C_{22}H_{24}N_2O_4Si_2$: 593. Found: 593.

5.4.11. *N*-{4-[4-(4-Formylamino-phenylethynyl)-3,2′-dinitro-biphenylethynyl]-phenyl}-formamide (15). 4,4′-Diethynyl-2,3′-dinitro-biphenyl (**13**) (1.25 g, 4.28 mmol) was coupled with *N*-(4-iodo-phenyl)-formamide (**9**)[30] (2.22 g, 8.99 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone)palladium(0) (0.123 g, 0.214 mmol), copper(I) iodide (0.082 g, 0.43 mmol), triphenylphosphine (0.226 g, 0.86 mmol), THF (25 mL), and DIEA (4.5 mL, 25.7 mmol). The reaction was stirred at 55°C for 4 h. The tube was filled with solid that was filtered and washed with CH_2Cl_2 to remove salts and starting materials to afford the desired product (2.13 g, 94% yield): mp 240°C (decomp.). (The desired product has poor solubility in most common organic solvents due to the hydrogen bonding nature of the formamides. The presence of two formamide groups allows the molecules to become a hydrogen-bonded polymer, thus, having poor solubility.) IR (KBr) 3362.2, 3231.9, 3073.1, 2883.6, 2204.7, 1690.4, 1601.0, 1521.3, 1406.2, 1336.6, 1285.9, 1245.0, 1144.1, 836.9, 691.9, 533.1 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 10.47 (d, J=9.1 Hz, 1.4H), 10.40 (t, J=9.4 Hz, 0.49H), 8.93 (d, J=10.4 Hz, 0.44H), 8.33 (s, 1.5H), 8.26 (d, J=17.1 Hz, 2H), 7.97 (d, J=7.8 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.79 (d, J=8.0 Hz, 1.16H), 7.72–7.68 (m, 4H), 7.61–7.55 (m, 4H), 7.32 (m, 1H).

5.4.12. 4,4′-Bis-(4-isocyano-phenylethynyl)-2,3′-dinitro-biphenyl (16). To a 500 mL round bottom flask was

added *N*-{4-[4-(4-formylamino-phenylethynyl)-3,2′-dinitro-biphenylethynyl]-phenyl}-formamide (**15**) (1.00 g, 1.89 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (200 mL) and triethylamine (20 mL) was added and the solution was cooled to 0°C. Triphosgene (0.560 g, 1.89 mmol) was then added. After 30 min starting material remained by TLC. An additional 0.280 g (0.95 mmol) of triphosgene was added. After 60 min an additional 0.280 g (0.95 mmol) of triphosgene was added. After 40 min an additional amount of triphosgene (0.280 g, 0.95 mmol) was added. After 2.25 h (total time), the reaction was warmed to ambient temperature. An additional 0.25 equiv. of triphosgene (0.140 g, 0.48 mmol) was added and stirred for 1.5 h. The solvents were then removed under reduced pressure. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) afforded the product (0.478 g, 51% yield): mp 140–150°C (decomp.). IR (KBr) 2122.8, 1531.5, 1505.5, 1338.1, 841.9, 528.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=1.6 Hz, 1H), 8.10 (d, J=1.8 Hz, 1H), 7.81 (dd, J=7.9, 1.6 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.62 (dt, J=8.4, 1.9 Hz, 2H), 7.58 (dt, J=8.4, 1.9 Hz, 2H), 7.53 (dd, J=7.9, 1.8 Hz, 1H), 7.46 (d, J=8.0 Hz, 1H), 7.41–7.38 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 166.9, 150.0, 148.8, 138.6, 136.1, 135.3, 133.7, 133.5, 133.3, 132.8, 132.4, 128.2, 127.1, 127.1, 125.2, 124.9, 124.0, 123.7, 118.6, 96.9, 91.9, 89.1, 87.3. LRMS calcd for $C_{30}H_{14}N_4O_4$: 494.1 Found: 494.0.

5.4.13. 4,4′-Dibromo-2,2′-dinitro-biphenyl (17).[13] 2,5-Dibromonitrobenzene (18.0 g, 64.1 mmol), copper powder (9.00 g, 141 mmol), DMF (120 mL), and a stir bar were added to a 250 mL round bottom flask equipped with a West condenser. The flask was heated in a 120°C oil bath for 2 h. The solution was filtered and diluted with water to precipitate yellow-brown crystals. Flash chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded pale yellow crystals (4.8 g, 75% yield): mp 149–150°C (lit. mp 146–148°C).[13] ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=2.0 Hz, 2H), 7.81 (dd, J=8.2, 2.0 Hz, 2H), 7.14 (d, J=8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ147.8, 137.0, 132.5, 132.4, 128.5, 123.3.

5.4.14. (4′-Bromo-2,2′-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (18). 4,4′-Dibromo-2,2′-dinitrobiphenyl (**17**) (4.00 g, 9.95 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.211 g, 0.300 mmol), copper(I) iodide (0.114 g, 0.597 mmol), THF (20 mL), DIEA (6.9 mL, 40 mmol), and TMSA (1.49 mL, 10.5 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 5 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product as a viscous brown oil (1.923 g, 46% yield). IR (KBr) 3083.4, 2958.5, 2899.0, 2868.3, 2177.0, 1530.8, 1346.2, 1249.7, 845.4, 760.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J=2.0 Hz, 1H), 8.26 (d, J=1.6 Hz, 1H), 7.79 (dd, J=8.1, 2.0 Hz, 1H), 7.71 (dd, J=7.9, 1.7 Hz, 1H), 7.19 (d, J=8.1 Hz, 1H), 7.14 (d, J=8.1 Hz, 1H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.2, 137.0, 136.8, 133.2, 133.0, 132.5, 131.2, 128.5, 128.4, 125.6, 123.1, 102.0, 99.4, 0.1. HRMS calcd for $C_{17}H_{15}N_2O_4BrSi$: 417.9985. Found: 417.9989 (Error=1.0 ppm).

5.4.15. (2,2′-Dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (19). (4′-Bromo-2,2′-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (**18**) (1.91 g, 4.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.136 mmol), copper(I) iodide (0.052 g, 0.273 mmol), THF (20 mL), DIEA (3.2 mL, 18 mmol), and phenylacetylene (0.60 mL, 5.5 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 1 d, followed by heating to 50°C for 2 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product as a yellow-brown solid (1.54 g, 77% yield): 143–146°C. IR (KBr) 3083.4, 2957.7, 2888.8, 2207.7, 2161.6, 1529.3, 1349.0, 1249.4, 1217.1, 1004.2, 843.8, 756.2, 689.2, 517.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J=1.5 Hz, 1H), 8.28 (d, J=1.5 Hz, 1H), 7.76 (dd, J=7.9, 1.6 Hz, 1H), 7.71 (dd, J=7.9, 1.5 Hz, 1H), 7.56 (m, 2H), 7.37 (m, 3H), 7.22 (d, J=7.9 Hz, 1H), 7.21 (d, J=7.9 Hz, 1H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 147.3, 136.8, 136.4, 133.8, 133.4, 132.3, 131.4, 131.3, 129.7, 129.0, 128.5, 128.0, 125.6, 125.4, 122.5, 102.2, 99.2, 93.3, 87.0, 0.2. HRMS calcd for $C_{25}H_{20}N_2O_4Si$: 440.1192. Found: 440.1187 (Error=1.3 ppm).

5.4.16. 4′-Ethynyl-2,2′-dinitro-4-phenylethynyl-biphenyl (20). (2,2′-Dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-trimethyl-silane (**19**) (1.50 g, 3.41 mmol), potassium carbonate (1.89 g, 13.7 mmol), methanol (20 mL), and CH_2Cl_2 (20 mL) were used following the general procedure for deprotection to afford the desired product as a viscous brown oil (1.21 g, 97% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J=1.6 Hz, 1H), 8.31 (d, J=1.6 Hz, 1H), 7.77 (m, 2H), 7.57 (m, 2H), 7.38 (m, 3H), 7.25 (m, 2H), 3.27 (s, 1H).

5.4.17. Thioacetic acid *S*-[4-(2,2′-dinitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl] ester (21). 4′-Ethynyl-2,2′-dinitro-4-phenylethynyl-biphenyl (**20**) (1.21 g, 3.30 mmol) was coupled with 4-thioacetyl-1-iodobenzene (**7**)[29] (0.917 g, 3.30 mmol) using the Pd/Cu cross coupling method described earlier using bis(dibenzylideneacetone)palladium(0) (0.380 g, 0.660 mmol), copper(I) iodide (0.126 g, 0.660 mmol), triphenylphosphine (0.433 g, 1.65 mmol), THF (25 mL), and DIEA (1.15 mL, 6.60 mmol) in a 100 mL round bottom flask under nitrogen. The solution was stirred in a 40°C oil bath for 1 d. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded the desired product as a green-yellow solid (1.23 g, 72% yield). IR (KBr) 3078.2, 2919.5, 2842.7, 2207.7, 1698.9, 1526.2, 1350.6, 1111.8, 1088.9, 826.4, 762.0, 691.1, 617.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=1.5 Hz, 2H), 7.79 (dd, J=8.0, 1.7 Hz, 2H), 7.58 (m, 4H), 7.43 (dt, 8.0, 1.7 Hz, 2H), 7.39 (m, 3H), 7.28 (d, J=8.0 Hz, 1H), 7.27 (d, J=7.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 147.5, 147.5, 136.5, 136.4, 134.7, 133.8, 133.4, 132.8, 132.3, 131.4, 131.3, 129.7, 129.6, 129.0, 128.2, 128.1, 125.7, 125.2, 126.6, 122.5, 93.3, 92.4, 88.4, 86.9, 30.8. HRMS calcd for $C_{30}H_{18}N_2O_5S$: 518.0936. Found: 518.0941 (Error=0.79 ppm).

5.4.18. 2,2′-Dinitro-4,4′-bis-trimethylsilanylethynyl-biphenyl (22). 2,2′-Dinitro-4,4′-dibromobiphenyl[13] (**17**)

(1.50 g, 3.73 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.131 g, 0.187 mmol), copper(I) iodide (0.071 g, 0.373 mmol), THF (20 mL), DIEA (5.20 mL, 29.8 mmol) and TMSA (1.32 mL, 9.33 mmol) were used following the general procedure for couplings. The tube was capped and heated in a 45°C oil bath for 3 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product (1.3 g, 80% yield): mp 82–90°C. IR (KBr) 3083.4, 2959.3, 2899.0, 2166.8, 1530.8, 1350.2, 1250.3, 1219.2, 930.2, 844.7, 753.3, 644.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J=1.6 Hz, 2H), 7.75 (dd, J=7.9, 1.7 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H), 0.31 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 136.5, 133.5, 131.0, 128.3, 125.2, 101.9, 99.0, −0.1. HRMS calcd for $C_{22}H_{24}N_2O_4Si_2$: 436.127465. Found: 436.126915. (Error=1.3 ppm).

5.4.19. 4,4′-Diethynyl-2,2′-dinitro-biphenyl (23). 2,2′-Dinitro-4,4′-bis-trimethylsilanylethynyl-biphenyl (**22**) (1.31 g, 3.00 mmol), potassium carbonate (2.49 g, 18.0 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were used following the general procedure for deprotection to afford the desired product (0.825 g, 94% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=1.5 Hz, 2H), 7.80 (dd, J=7.9, 1.6 Hz, 2H), 7.27 (d, J=7.9 Hz, 2H), 3.31 (s, 2H).

5.4.20. Thioacetic acid *S*-{4-[4′-(4-acetylsulfanyl-phenylethynyl)-2,2′-dinitro-biphenyl-4-ylethynyl]-phenyl} ester (24). 4,4′-Diethynyl-2,2′-dinitro-biphenyl (**23**) (0.825 g, 2.82 mmol), bis(dibenzylideneacetone)palladium(0) (0.324 g, 0.564 mmol), copper(I) iodide (0.107 g, 0.564 mmol), triphenylphosphine (0.370 g, 1.41 mmol), THF (20 mL), DIEA (2.0 mL, 11.3 mmol), and 4-(thioacetyl)iodobenzene (**7**)[26] (1.65 g, 5.92 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 1 d. Flash column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.46) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as slightly yellow solid (0.434 g, 26% yield): mp 160–173°C (decomp.). IR (KBr) 3083.4, 2202.6, 1716.5, 1524.4, 1347.7, 1117.3, 828.6, 597.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=1.5 Hz, 2H), 7.83 (dd, J=8.0, 1.7 Hz, 2H), 7.62 (dt, J=8.5, 1.8 Hz, 4H), 7.47 (dt, J=8.5, 1.8 Hz, 4H), 7.32 (d, J=7.9 Hz, 2H), 2.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 147.4, 136.5, 134.7, 133.7, 132.8, 131.4, 129.7, 128.2, 125.3, 123.6, 92.4, 88.4, 30.8.

5.4.21. *N*-(2′-Acetyamino-4,4′-dibromo-biphenyl-2-yl)-acetamide (25). 4,4′-Dibromo-2,2′-dinitro-biphenyl (**17**) (5.75 g, 14.3 mmol), ethanol (70 mL) and concentrated HCl (25 mL) were added to a 250 mL round-bottom flask.[16] Tin powder (6.79 g, 57.2 mmol) was then added slowly while stirring. The mixture was then heated to reflux for 30 min before being poured into ice and water. The product was extracted with ethyl acetate and washed with NaOH (aq). The crude diamine was then placed in a 250 mL round-bottom flask with glacial acetic acid (6.2 mL) and a stir bar. Acetic anhydride (5.4 mL, 57.2 mmol) was then added and the solution was heated in a 70°C oil bath for 40 min. Water was then added and the mixture neutralized with NaOH (aq). The crude product was extracted with ethyl acetate. Column chromatography (silica gel using 1:1 CH_2Cl_2/ethyl acetate as eluent; R_f=0.46) afforded the desired compound (5.17 g, 85% yield): mp 127–129°C. IR (KBr) 3412.0, 3277.6, 3109.0, 3047.5, 3011.7, 1675.5, 1564.9, 1510.4, 1450.2, 1397.4, 1367.8, 1278.7, 1083.9, 1003.0, 879.6, 813.2, 686.1, 602.9, 502.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (br s, 2H), 7.35 (dd, J=8.2, 1.9 Hz, 2H), 7.01 (d, J=8.1 Hz, 2H), 6.91 (br s, 2H), 1.96 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.0, 132.0, 128.9, 127.4, 126.9, 123.8, 24.5. HRMS calcd for $C_{16}H_{14}N_2O_2Br_2$: 425.940305. Found: 425.940263 (Error=0.099 ppm).

5.4.22. *N*-(2′-Acetylamino-4,4′-dibromo-5,5′-dinitro-biphenyl-2-yl)-acetamide (26). To a 500 mL round-bottom flask was added conc. H_2SO_4 (85 mL) followed by the slow addition of *N*-(2′-acetyamino-4,4′-dibromo-biphenyl-2-yl)-acetamide (**25**) (8.90 g, 20.9 mmol). The mixture was cooled to −10°C and a solution of conc. H_2SO_4 (50 mL) and conc. HNO_3 (50 mL) was added slowly over 2.25 h. The mixture was allowed to warm to 10°C over 1 h before being poured onto ice and extracted with ethyl acetate. Column chromatography (silica gel using 2:1 CH_2Cl_2/ethyl acetate; R_f=0.49) afforded the desired compound (8.11 g, 75% yield): mp 252–254°C. IR (KBr) 3385.5, 3355.1, 3114.1, 3073.1, 3037.3, 1704.7, 1599.3, 1552.2, 1533.0, 1495.2, 1329.1, 1233.8, 1049.2, 1004.6, 839.3, 666.8 cm^{-1}. ^1H NMR (200 MHz, acetone-d_6) δ 9.03 (br s, 2H), 8.70 (m, 2H), 8.06 (s, 2H), 1.97 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6) δ 169.7, 145.5, 141.6, 129.2, 128.7, 128.6, 126.9, 115.1, 23.5. HRMS calcd for $C_{16}H_{12}Br_2N_4O_6$: 513.912380. Found: 513.912528 (Error=0.29 ppm).

5.4.23. 4,4′-Dibromo-5,5′-dinitro-biphenyl-2,2′-diamine (27). To a 100 mL round-bottom flask was added conc. H_2SO_4 (30 mL) followed slowly by *N*-(2′-acetylamino-4,4′-dibromo-5,5′-dinitro-biphenyl-2-yl)-acetamide (**26**) (1.0 g, 1.94 mmol). Water (20 mL) was then slowly added while stirring over 30 min (exotherm; temperature reached 90°C). The flask was placed in a 90°C oil bath for 1 h, at which point water (30 mL) was added and the reaction mixture cooled to ~50°C. The mixture was then poured onto ice and the solid was filtered to give the desired product as a yellow solid (0.805 g, 96% yield): mp >300°C. IR (KBr) 3463.3, 3375.0, 1628.5, 1586.0, 1541.8, 1500.5, 1297.9, 1250.1, 1116.9, 1060.6 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 7.94 (s, 2H), 7.23 (s, 2H), 6.01 (br s, 4H). ^{13}C NMR (125 MHz, acetone-d_6) δ 152.1, 130.9, 120.0, 119.2, 117.1. HRMS calcd for $C_{12}H_8N_4O_4Br_2$: 429.891251. Found: 429.891129 (Error=0.28 ppm).

5.4.24. 4′-Bromo-2,5,2′,5′-tetranitro-4-phenylethynyl-biphenyl (28) from 27. 4,4′-Dibromo-5,5′-dinitro-biphenyl-2,2′-diamine (**27**) (0.900 g, 2.08 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.073 g, 0.104 mmol), copper(I) iodide (0.040 g, 0.208 mmol), THF (25 mL), DIEA (1.45 mL, 8.32 mmol), and phenylacetylene (0.25 mL, 2.29 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 1 d. Flash column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; R_f=0.51) afforded an inseparable mixture of products and starting material (0.784 g) which was taken onto the next step. To a small plastic bottle with a stir bar was added acetonitrile (90 mL) and water (3 mL). The

solution was cooled to −25°C and 20% F_2 in He was bubbled through at 70 cc/min for 2.5 h. The F_2 flow was turned off and He was bubbled through for 15 min at 70 cc/min to remove any excess F_2. 4-Bromo-5,5′-dinitro-4-phenylethynyl-biphenyl-2,2′-diamine (0.784 g as a mixture from previous reaction) in acetone (10 mL) was then added to the solution and stirred for 2.5 min before being poured into a saturated sodium bicarbonate solution. The material was washed with water and extracted with CH_2Cl_2. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent) afforded the desired product as an orange solid (0.120 g, 11% yield over 2 steps). IR (KBr) 3098.7, 2202.6, 1544.6, 1341.8, 1265.4, 912.1, 835.3, 753.3, 681.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.62 (s, 1H), 8.08 (s, 1H), 7.88 (s, 1H), 7.69 (m, 2H), 7.48 (m, 3H). HRMS calcd for $C_{20}H_9N_4O_8Br$: 511.960386. Found: 511.959830 (Error=1.1 ppm).

5.4.25. Thioacetic acid *S*-[4-2,5,2′5′-tetranitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl] ester (30). 4′-Bromo-2,5,2′,5′-tetranitro-4-phenylethynyl-biphenyl (**28**) (0.110 g, 0.214 mmol), bis(dibenzylideneacetone)-palladium(0) (0.025 g, 0.043 mmol), copper(I) iodide (0.008 g, 0.043 mmol), triphenylphosphine (0.023 g, 0.086 mmol), THF (15 mL), DIEA (0.075 mL, 0.43 mmol), and 4-thioacetyl-1-ethynylbenzene[18] (**29**) (0.049 g, 0.278 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 2 h and then at 50°C for 1 h. Flash column chromatography (silica gel using 1:2 hexanes/CH_2Cl_2 as eluent) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as an orange solid (0.031 g, 24% yield): mp 130–150°C (decomp.). IR (KBr) 3073.1, 2212.7, 1707.9, 1548.8, 1340.8, 1270.9, 1118.3, 912.1, 829.3, 759.1, 681.6, 615.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 2H), 8.13 (s, 1H), 8.11 (s, 1H), 7.70 (m, 4H), 7.49 (m, 5H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.00, 151.13, 148.49, 134.59, 133.08, 132.68, 131.71, 131.42, 131.23, 131.14, 130.71, 128.94, 127.65, 127.55, 122.27, 121.62, 121.29, 121.17, 102.87, 101.60, 84.11, 82.88, 30.64.

5.4.26. 4,4′-Dibromo-biphenyl-2,3′-diamine. 4,4′-Dibromo-2,3′-dinitro-biphenyl[13] (3) (6.10 g, 15.2 mmol) was added to a 250 mL round bottom flask containing concentrated HCl (30 mL), EtOH (80 mL) and a stir bar. Tin powder (7.21 g, 60.7 mmol) was slowly added to the solution with stirring. The solution was heated to reflux for 30 min and then poured into ice water. The mixture was extracted with ethyl acetate and washed with 50% NaOH (aq). Removal of the solvent provided the crude product, which was taken onto the next step with no further purification (5.28 g): mp 87–90°C. IR (KBr) 3423.0, 3408.6, 3324.0, 3304.2, 3190.9, 1616.1, 1590.3, 1559.6, 1478.1, 1402.1, 1301.3, 1241.3, 1037.4, 908.9, 799.8, 661.8, 461.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=8.1 Hz, 1H), 6.91 (m, 2H), 6.86 (m, 1H), 6.75 (d, J=2.0 Hz, 1H), 6.64 (dd, J=8.1, 2.0 Hz, 1H), 4.18 (br s, 2H), 3.84 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 145.0, 139.2, 133.5, 131.8, 126.0, 122.6, 121.8, 120.3, 118.5, 116.4, 108.8. HRMS calcd for $C_{12}H_{10}N_2Br_2$: 341.919157. Found: 341.918664 (Error=1.4 ppm).

5.4.27. *N*-(3′-Acetylamino-4,4′-dibromo-biphenyl-2-yl)-acetamide (31). 4,4′-Dibromo-biphenyl-2,3′-diamine (5.28 g, 12.4 mmol) and acetic acid (6.8 mL) were added to a 100 mL round bottom flask followed by acetic anhydride (5.73 mL, 60.7 mmol). The flask was placed in a 70°C oil bath for 40 min. The solution was neutralized with 50% NaOH (aq) and extracted with CH_2Cl_2. Removal of the solvent gave the desired product (6.47 g, 100% over 2 steps). mp: 168–171°C. IR (KBr) 3386.2, 3260.8, 3022.9, 1685.9, 1575.7, 1510.2, 1449.5, 1386.2, 1275.8, 1050.3, 1025.8, 806.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (br s, 1H), 8.22 (br s, 1H), 7.68 (m, 2H), 7.50 (br s, 1H), 7.30 (dd, J=8.2, 1.7 Hz, 1H), 7.11 (d, J=8.2 Hz, 1H), 6.99 (dd, J=8.2, 2.2 Hz, 1H), 2.28 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.9, 137.7, 136.2, 133.7, 131.4, 129.6, 127.8, 126.5, 125.1, 123.6, 123.0, 114.0, 25.8, 25.0. HRMS calcd for $C_{16}H_{14}N_2O_2Br_2$: 425.940266. Found: 425.939783 (Error=1.1 ppm).

5.4.28. *N*-(5′-Acetylamino-4,4′-dibromo-5,2′-dinitro-biphenyl-2-yl)-acetamide (32). To a 500 mL round bottom flask was added *N*-(3-acetylamino-4,4-dibromo-biphenyl-2-yl)-acetamide (**31**) (2.45 g, 5.75 mmol), CH_2Cl_2 (20 mL) and conc. H_2SO_4 (70 mL) and the mixture was cooled to −15°C. Next, an ice cold solution of HNO_3 (15 mL, 70%) and conc. H_2SO_4 (15 mL) were added dropwise over 1 h. The mixture was allowed to warm to 0°C over 2 h at which point the reaction was poured onto ice and washed with water and ethyl acetate. Column chromatography (silica gel using 3:1 CH_2Cl_2/ethyl acetate; R_f=0.21) afforded the desired product (1.29 g, 43% yield): mp 229–232°C. IR (KBr) 3387.3, 3338.3, 1699.0, 1570.7, 1533.1, 1507.5, 1466.7, 1371.3, 1335.1, 1236.9, 1074.0, 895.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (br s, 2H), 7.33 (dd, J=8.2, 2.0 Hz, 2H), 7.15 (br s, 2H), 6.98 (d, J=8.2 Hz, 2H), 1.92 (s, 6H). ^{13}C NMR (125 MHz, acetone-d_6) δ 169.6, 169.4, 144.9, 143.9, 142.1, 141.1, 130.9, 130.2, 129.3, 127.6, 127.1, 125.6, 114.7, 113.7, 24.0, 23.6. HRMS calcd for $C_{16}H_{12}Br_2N_4O_6$: 515.910536. Found: 515.910650 (Error=0.22 ppm).

5.4.29. 4,4′-Dibromo-5,6′-dinitro-biphenyl-2,3′-diamine (33). To a 100 mL round-bottom flask was added *N*-(5′-acetylamino-4,4′-dibromo-5,2′-dinitro-biphenyl-2-yl)-acetamide (**32**) (0.441 g, 0.854 mmol), 3N HCl (20 mL), and THF (20 mL). The solution was heated to reflux for 3 h before being neutralized with NaOH and extracted with ethyl acetate to give the desired product as a yellow solid (0.356 g, 96% yield): mp 250–270°C (decomp.). IR (KBr) 3472.6, 3446.7, 3353.5, 3234.0, 1624.4, 1588.7, 1556.8, 1496.9, 1300.5, 1255.8, 1126.4, 1055.6, 903.1, 841.6 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 8.34 (s, 1H), 7.84 (s, 1H), 7.17 (s, 1H), 6.82 (s, 1H), 6.30 (br s, 2H), 5.90 (br s, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 151.8, 151.7, 137.7, 137.6, 133.5, 131.2, 128.1, 123.7, 119.1, 117.2, 116.5, 106.1.

5.4.30. 4′-Bromo-2,5,2′,5′-tetranitro-4-phenylethynyl-biphenyl (28) from 33. 4,4′-Dibromo-5,6′-dinitro-biphenyl-2,3′-diamine (**33**) (1.04 g, 2.41 mmol) and phenylacetylene (0.290 mL, 2.65 mmol) were coupled following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.085 g, 0.121 mmol), copper(I)

iodide (0.046 g, 0.241 mmol), THF (20 mL), and DIEA (1.7 mL, 9.64 mmol). The tube was capped and the solution was stirred in a 40°C oil bath for 1.5 h. The temperature was then increased to 50°C for 1 d. Flash column chromatography (silica gel using 1:1 ethyl acetate/hexanes as eluent; R_f=0.42) followed by precipitation from acetone/hexanes afforded the desired product (0.780 g, ~72% yield) which was taken directly onto the oxidation step.[17] 0.300 g (0.662 mmol) of this compound was dissolved in THF (10 mL). Acetonitrile (90 mL) and water (3 mL) were placed in a plastic bottle and cooled to −45°C. A 20% mixture of F_2 in He was bubbled through at 60 cc/min for 2.5 h. Helium was then bubbled through for 20 min at 60 cc/min. Added the THF solution and stirred for 2.5 min. The reaction mixture was then poured into $NaHCO_3$ (aq) and extracted with CH_2Cl_2. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent; R_f=0.46) afforded the desired tetranitro product (0.180 g, 45% over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.58 (s, 1H), 8.04 (s, 1H), 7.84 (s, 1H), 7.65 (m, 2H), 7.43 (m, 3H). HRMS calcd for $C_{20}H_9BrN_4O_8$: 511.960396. Found: 511.959296 (Error=2.1 ppm).

5.4.31. 4-Iodo-2-nitro-phenylamine (34).[32] 2-Nitroaniline (30.0 g, 217 mmol), sodium acetate (18.7 g, 228 mmol) and acetic acid (150 mL) were added to a 500 mL round bottom flask with a stir bar. To this flask was added a solution of iodine monochloride (37.0 g, 228 mmol) in acetic acid (100 mL) and the resulting solution was heated at 80°C for 30 min. The solution was immediately poured into water (600 mL) and allowed to stand for 3 h. The orange solid was filtered to give the desired product (54.5 g, 95%): mp 121–124°C (lit[20]: mp 121–123°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=2.1 Hz, 1H), 7.54 (dd, J=8.8, 2.1 Hz, 1H), 6.59 (d, J=8.8 Hz, 1H), 6.09 (br s, 2H).

5.4.32. 2-Nitro-4-phenylethynyl-phenylamine (35). 4-Iodo-2-nitro-phenylamine (**34**) (10.0 g, 37.9 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.266 g, 0.379 mmol), copper(I) iodide (0.144 g, 0.758 mmol), DIEA (19.8 mL, 114 mmol), THF (35 mL) and phenylacetylene (4.6 mL, 37.9 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at RT for 2.5 h. Precipitation from CH_2Cl_2/hexanes followed by extraction with Et_2O and water afforded the desired product (7.93 g, 88% yield): mp 162–163°C. IR (KBr) 3470.7, 3342.1, 1641.5, 1598.7, 1552.2, 1516.3, 1411.5, 1340.5, 1234.8, 1142.8, 833.7, 756.2, 687.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J=2.0 Hz, 1H), 7.52 (m, 3H), 7.38 (m, 3H), 6.81 (dd, J=8.6, 0.4 Hz, 1H), 6.24 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 138.7, 132.2, 131.9, 129.9, 128.8, 128.7, 123.4, 119.3, 112.5, 89.1, 88.0. HRMS calcd for $C_{14}H_{10}N_2O_2$: 238.074228. Found: 238.074109 (Error=0.50 ppm).

5.4.33. 1-Iodo-2-nitro-4-phenylethynyl-benzene (36). To a 500 mL round bottom flask (cooled to −20 to −30°C) was added $BF_3{\cdot}OEt_2$ (16.8 mL, 132 mmol) followed by 2-nitro-4-phenylethynyl-phenyamine (**35**) (7.89 g, 33.1 mmol) in THF (55 mL) over 15 min. Next, t-BuONO (13.8 mL, 115.9 mmol) in THF (45 mL) was added over 20 min. The solution was allowed to warm to 0°C over 25 min and Et_2O was added to effect precipitation of the diazonium salt. The salt was filtered and washed with cold Et_2O to afford 10.92 g of solid. To a 500 mL round bottom flask was added acetonitrile (125 mL), NaI (9.92 g, 66.2 mmol) and I_2 (8.4 g, 33.1 mmol). The diazonium salt was then slowly added to this solution over 15 min. The solution was washed with $Na_2S_2O_3$ (aq) and extracted with CH_2Cl_2 to afford the desired product which needed no further purification (9.78 g, 85% yield): mp 114–116°C. IR (KBr) 3078.2, 3047.5, 2211.9, 1522.2, 1439.3, 1351.6, 1014.3, 891.6, 824.3, 755.0, 686.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J=8.2 Hz, 1H), 7.96 (d, J=1.9 Hz, 1H), 7.52 (m, 2H), 7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.0, 132.2, 129.7, 129.0, 128.4, 125.4, 122.4, 93.7, 86.6, 85.9. HRMS calcd for $C_{14}H_8NO_2I$: 348.959973. Found: 348.959869 (Error=0.30 ppm).

5.4.34. Trimethyl-(4-tributylstannanyl-phenylethynyl)-silane (37). To a 500 mL round-bottom flask was added (4-bromo-phenylethynyl)-trimethyl-silane[21] (3.63 g, 14.3 mmol) and a stir bar. Air was removed and N_2 backfilled (3×). THF (50 mL) was added and the solution cooled to 78°C. Next, n-BuLi (6.22 mL of a 2.53 M solution) was added dropwise over 15 min. The solution was stirred for 10 min. Tributyltin chloride (4.46 mL, 16.4 mmol) in THF (10 mL) was then added over 15 min. The reaction was allowed to warm to room temperature overnight before washing with NaCl (aq) and CH_2Cl_2. Column chromatography (silica gel using hexanes as eluent; R_f=0.65) followed by Kugelrohr distillation (150°C at 1.5 mm Hg) removed the impurities and left the desired product as an oil (4.53 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 4H), 1.50 (m, 6H), 1.29 (m, 6H), 1.03 (m, 6H), 0.86 (m, 9H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.7, 136.6, 136.4, 131.6, 131.4, 131.2, 122.9, 105.9, 94.5, 29.6, 29.4, 29.3, 28.0, 27.7, 27.5, 14.1, 11.7, 11.6, 10.0, 8.4, 8.3, 0.4.

5.4.35. Trimethyl-(2′-nitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-silane (39). 1-Iodo-2-nitro-4-phenylethynyl-benzene (**36**) (3.41 g, 9.78 mmol), bis(dibenzylideneacetone)palladium(0) (0.112 g, 0.200 mmol), and triphenylarsine (0.122 g, 0.400 mmol) were placed in a screw cap tube.[22] Air was removed and N_2 backfilled (3×). Trimethyl-(4-tributylstannanyl-phenylethynyl)-silane (**38**) (3.41 g, 9.78 mmol) and THF (35 mL) were then added. The tube was capped and placed in a 80°C oil bath for 19 h. The mixture was washed with NaCl (aq) and diethyl ether. Column chromatography (silica gel using 3:1 hexanes/CH_2Cl_2 as eluent; R_f=0.50) afforded the desired product (2.59 g, 67% yield): mp 107–110°C. IR (KBr) 3062.5, 2962.5, 2157.0, 1533.1, 1492.8, 1355.6, 1248.3, 855.1, 829.0, 762.8, 694.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=1.6 Hz, 1H), 7.71 (dd, J=8.0, 1.6 Hz, 1H), 7.55 (m, 2H), 7.51 (dt, J=8.3, 1.8 Hz, 2H), 7.37 (m, 4H), 7.25 (dt, J=8.3, 1.7 Hz, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.3, 135.4, 135.4, 132.7, 132.2, 129.5, 128.9, 128.2, 127.5, 124.6, 123.9, 122.6, 104.8, 96.3, 92.9, 87.1, 0.3. HRMS calcd for $C_{25}H_{21}SiNO_2$: 395.134158. Found: 395.134321 (Error=0.41 ppm).

5.4.36. 4′-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (40). Trimethyl-(2′-nitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-silane (**39**) (2.52 g, 6.37 mmol), potassium

carbonate (2.64 g, 19.1 mmol), methanol (25 mL), and CH_2Cl_2 (25 mL) were used following the general deprotection method to afford the product (2.03 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J=1.7 Hz, 1H), 7.72 (dd, J=8.0, 1.7 Hz, 1H), 7.56–7.52 (m, 4H), 7.40–7.36 (m, 4H), 7.27 (dt, J=8.5, 1.8 Hz, 2H), 3.13 (s, 1H).

5.4.37. Thioacetic acid *S*-[4-(2′-nitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl] ester (41). 4′-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (**40**) (1.00 g, 3.09 mmol), bis(dibenzylideneacetone)palladium(0) (0.089 g, 0.155 mmol), copper(I) iodide (0.059 g, 0.31 mmol), triphenylphosphine (0.162 g, 0.620 mmol), THF (15 mL), DIEA (2.15 mL, 12.4 mmol), and 4-(thioacetyl)iodobenzene (**7**)[26] (0.859 g, 3.09 mmol) were used following the general procedure for couplings. The tube was capped and the solution was stirred at ambient temperature for 16 h. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.47) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as a yellow solid (0.982 g, 67% yield): mp 134–136°C. IR (KBr) 3057.4, 2202.1, 1707.2, 1527.3, 1494.8, 1350.1, 1111.0, 1085.5, 1003.7, 953.9, 829.3, 758.0, 688.8, 606.1, 545.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J=1.6 Hz, 1H), 7.73 (dd, J=8.0, 1.6 Hz, 1H), 7.55 (m, 6H), 7.39 (m, 6H), 7.37 (m, 4H), 7.31 (dt, J=8.3, 1.7 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 149.4, 137.3, 135.4, 134.7, 132.7, 132.5, 132.2, 129.6, 129.0, 128.7, 128.4, 127.6, 124.7, 124.6, 123.7, 122.6, 93.0, 90.9, 90.4, 87.1, 30.8.

5.4.38. *N*-[4-(2′-Nitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide (42). 4′-Ethynyl-2-nitro-4-phenylethynyl-biphenyl (**40**) (1.01 g, 3.12 mmol) was coupled with *N*-(4-iodo-phenyl)-formamide (**9**)[30] (0.771 g, 3.12 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone)palladium(0) (0.090 g, 0.156 mmol), copper(I) iodide (0.059 g, 0.31 mmol), triphenylphosphine (0.162 g, 0.62 mmol), DIEA (2.2 mL, 12.5 mmol), and THF (15 mL). After stirring at room temperature for 18 h, the reaction mixture was washed with NH_4Cl (aq) and CH_2Cl_2. Column chromatography (silica gel using CH_2Cl_2 followed by 1:1 CH_2Cl_2/ethyl acetate as eluent; R_f=0.66) afforded the desired compound (1.28 g, 93% yield): mp 190–200°C (decomp.). IR (KBr) 1687.6, 1603.4, 1522.4, 1352.5, 1298.0, 838.4, 756.6, 691.9 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J=11.4 Hz, 0.4H), 8.39 (d, J=1.6 Hz, 0.6H), 8.00 (m, 1H), 7.72 (m, 1H), 7.54 (m, 7H), 7.48 (br s, 0.22H), 7.45 (br s, 0.22H), 7.42 (d, J=7.9 Hz, 1H), 7.38 (m, 3H), 7.30 (m, 2H), 7.15 (br s, 0.6H), 7.05 (m, 0.82H). HRMS calcd for $C_{29}H_{18}N_2O_3$: 442.131742. Found: 442.132230 (Error=1.1 ppm).

5.4.39. 4′-(4-Isocyano-phenylethynyl)-2-nitro-4-phenylethynyl-biphenyl (43). To a 50 mL round bottom flask was added *N*-[4-(2′-nitro-4′-phenylethynyl-biphenyl-4-ylethynyl)-phenyl]-formamide (**42**) (0.500 g, 1.13 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (25 mL) and triethylamine (5 mL) were added and the tube was cooled to 0°C. Triphosgene (0.152 g, 0.570 mmol) was then added. After 30 min starting material remained by TLC. An additional 0.076 g (0.285 mmol) of triphosgene was added. After 30 min (1 h total time), the reaction was complete by TLC. The mixture was washed with water and CH_2Cl_2. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.84) afforded the product (0.348 g, 73% yield): 180–190°C (decomp.). IR (KBr) 3052.6, 2121.2, 1540.9, 1523.3, 1501.1, 1348.1, 999.2, 834.2, 760.2, 692.7, 538.3 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J=1.4 Hz, 1H), 7.73 (dd, J=8.0, 1.8 Hz, 1H), 7.56 (m, 6H), 7.41 (d, J=8.2 Hz, 1H), 7.37 (m, 5H), 7.31 (dt, J=8.5, 1.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.4, 137.7, 135.4, 135.3, 133.1, 132.5, 132.2, 129.6, 129.0, 128.4, 127.6, 126.9, 126.4, 125.0, 124.8, 123.2, 122.6, 93.0, 92.0, 89.4, 87.0. HRMS calcd for $C_{29}H_{16}N_2O_2$: 424.121178. Found: 424.121021 (Error=0.37 ppm).

5.4.40. 4-Bromo-5,5′-dinitro-4′-trimethylsilanylethynyl-biphenyl-2,2′-diamine. 4,4′-Dibromo-5,5′-dinitro-biphenyl-2,2′-diamine (**27**) (2.49 g, 5.76 mmol) was coupled with TMSA (1.06 mL, 7.49 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.202 g, 0.288 mmol), copper(I) iodide (0.110 g, 0.576 mmol), THF (75 mL), and DIEA (4.0 mL, 23.04 mmol). The tube was capped and the solution was heated in a 45°C oil bath for 3 h. Flash column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; R_f=0.65) afforded the impure desired product (1.44 g, ~80% pure) which was taken directly onto the next step. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.98 (d, J=1.1 Hz, 1H), 7.95 (d, J=1.1 Hz, 1H), 7.25 (m, 1H), 7.09 (m, 1H), 5.98 (br s, 2H), 5.94 (br s, 2H), 0.20 (s, 9H).

5.4.41. 5,5′-Dinitro-4-phenylethynyl-4′-trimethylsilanylethynyl-biphenyl-2,2′-diamine (44). Crude 4-bromo-5,5′-dinitro-4′-trimethylsilanylethynyl-biphenyl-2,2′-diamine (from the previous reaction; 1.44 g, ~2.56 mmol) was coupled with phenylacetylene (0.46 mL, 4.16 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)-palladium(II) dichloride (0.112 g, 0.160 mmol), copper(I) iodide (0.061 g, 0.320 mmol), THF (30 mL), and DIEA (2.2 mL, 12.8 mmol). The tube was capped and the solution was heated in a 50°C oil bath for 16 h. Flash column chromatography (silica gel using 1:1 hexanes/ethyl acetate as eluent; R_f=0.59) afforded the desired product (0.937 g, 35% yield over 2 steps). IR (KBr) 3457.2, 3366.9, 1621.2, 1541.7, 1504.0, 1311.1, 1252.7, 845.6, 755.8 cm^{-1}. ^{1}H NMR (200 MHz, acetone-d_6) δ 8.04 (s, 1H), 8.00 (s, 1H), 7.61 (m, 2H), 7.47 (m, 3H), 7.16 (s, 1H), 7.09 (s, 1H), 5.96 (br s, 2H), 5.94 (br s, 2H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, acetone-d_6) δ 151.6, 151.5, 139.0, 138.7, 132.1, 129.7, 129.6, 129.5, 129.1, 123.2, 120.9, 120.6, 120.4, 120.3, 119.6, 101.7, 101.4, 95.5, 86.6, −0.7. HRMS calcd for $C_{25}H_{22}N_4O_4Si$: 470.141034. Found: 470.141303 (Error=0.57 ppm).

5.4.42. 4′-Ethynyl-5,5′-dinitro-4-phenylethynyl-biphenyl-2,2′-diamine (45). 5,5′-Dinitro-4-phenylethynyl-4′-trimethylsilanylethynyl-biphenyl-2,2′-diamine (**44**) (1.38 g, 2.93 mmol), potassium carbonate (1.62 g, 11.7 mmol), methanol (100 mL), CH_2Cl_2 (50 mL), and THF (50 mL) were used following the general deprotection method described earlier. A short silica plug (using 1:1 hexanes/ethyl acetate; R_f=0.42) afforded the desired product (0.934 g, 80% yield). ^{1}H NMR (200 MHz,

acetone-d_6) δ 8.05 (s, 1H), 8.01 (s, 1H), 7.61 (m, 2H), 7.47 (m, 3H), 7.16 (s, 1H), 7.13 (s, 1H), 5.98 (br s, 4H), 4.08 (s, 1H).

5.4.43. Thioacetic acid *S*-[4-(2,2-diamino-5,5-dinitro-4-phenylethynyl-biphenyl-4-ylethynyl)-phenyl] ester (46). 4′-Ethynyl-5,5′-dinitro-4-phenylethynyl-biphenyl-2,2′-diamine (**45**) (0.934 g, 2.34 mmol), bis(dibenzylideneacetone)palladium(0) (0.067 g, 0.117 mmol), copper(I) iodide (0.045 g, 0.234 mmol), triphenylphosphine (0.123 g, 0.468 mmol), THF (20 mL), DIEA (1.63 mL, 9.36 mmol), and 4-(thioacetyl)iodobenzene (**7**) (0.716 g, 2.57 mmol) were used following the general procedure for couplings. The tube was placed in a 50°C oil bath for 15 h. Column chromatography (silica gel using 1:1 hexanes/ethyl acetate; R_f=0.45) followed by precipitation from acetone/hexanes and CH_2Cl_2/hexanes afforded the desired product as a yellow-green solid (0.460 g, 36% yield): mp 200–208°C (decomp.). IR (KBr) 3463.1, 3360.6, 3237.0, 3047.5, 2207.7, 1690.5, 1622.6, 1602.0, 1538.1, 1504.7, 1302.8, 1254.8, 1096.4, 819.9, 743.1 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6) δ 8.08 (s, 1H), 8.07 (s, 1H), 7.68 (dt, J=8.3, 1.8 Hz, 2H), 7.62 (m, 2H), 7.53 (dt, J=8.4, 1.8 Hz, 2H), 7.47 (m, 3H), 7.19 (s, 1H), 7.18 (s, 1H), 5.98 (br d, J=8.8 Hz, 4H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 192.5, 151.7, 151.6, 138.7, 138.7, 134.9, 132.6, 132.1, 130.1, 129.8, 129.7, 129.6, 129.1, 124.2, 123.2, 120.9, 120.5, 120.5, 120.3, 119.8, 119.7, 95.5, 94.5, 88.1, 86.6, 29.8.

5.4.44. 2,7-Dibromo-9*H*-fluorene (47).[23] To a 1 L round-bottom flask, wrapped in aluminum foil, was added fluorene (50.0 g, 300.8 mmol) and $CHCl_3$ (450 mL). The solution was cooled to 0°C and ferric chloride (0.716 g, 4.5 mmol) was added. Bromine (32.6 mL, 632 mmol) was added slowly over 15 min at which point the ice bath was removed and the solution allowed to warm slowly over 3 h. The mixture was washed with $Na_2S_2O_3$ (aq) and extracted with $CHCl_3$ followed by drying with $MgSO_4$ to afford the desired product (98.1 g, 100% yield): mp 161–164°C (lit. mp 163.5–165.5°C[33]). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.55 (d, J=8.1 Hz, 2H), 7.47 (m, 2H), 3.81 (s, 2H).

5.4.45. 2,7-Dibromo-4-nitro-9*H*-fluorene (48).[24] To a 250 mL round-bottom flask was added 2,7-dibromo-9*H*-fluorene (**47**) (10.0 g, 30.7 mmol) and glacial acetic acid (125 mL). The solution was heated to 35°C and a solution of HNO_3 (7 mL) and H_2SO_4 (7 mL) was added slowly over 20 min. The mixture was stirred for 5 min and then heated to 70°C for 15 min. After cooling to room temperature, a yellow solid was filtered and washed with water. Recrystallization from ethanol/toluene afforded the desired product as yellow crystals (7.15 g, 63% yield): mp 192–193°C (lit[24] mp 194.5–195.5°C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=1.4 Hz, 1H), 7.92 (d, J=8.6 Hz, 1H), 7.87 (br s, 1H), 7.71 (br s, 1H), 7.53 (m, 1H), 3.96 (s, 2H).

5.4.46. 4-Nitro-2,7-bis-trimethylsilanylethynyl-9*H*-fluorene (49). 2,7-Dibromo-4-nitro-9*H*-fluorene (**48**) (1.00 g, 2.70 mmol) was coupled with TMSA (0.42 mL, 3.0 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.270 mmol), THF (20 mL), and DIEA (1.9 mL, 10.8 mmol). The tube was capped and the solution was stirred at room temperature for 1 d. More TMSA was added (0.76 mL, 5.4 mmol) and the tube was placed in a 55°C oil bath for 15 h. Flash column chromatography (silica gel using 3:1 hexanes/CH_2Cl_2 as eluent; R_f=0.51) afforded the desired product (0.709 g, 65% yield): mp 221–224°C. IR (KBr) 3077.9, 3052.3, 2959.7, 2898.7, 2150.8, 1517.0, 1449.8, 1356.2, 1248.3, 980.3, 938.1, 842.2, 759.3, 701.1, 655.4, 424.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.77 (d, J=1.4 Hz, 1H), 7.64 (m, 1H), 7.47 (m, 1H), 3.90 (s, 2H), 0.262 (s, 9H), 0.258 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.2, 144.8, 137.3, 134.1, 132.6, 131.7, 128.6, 127.2, 125.1, 124.1, 122.7, 105.3, 103.0, 98.1, 96.7, 37.0, 0.3, 0.2. HRMS calcd for $C_{23}H_{25}NO_2Si_2$: 403.142387. Found: 403.142344 (Error=0.11 ppm).

5.4.47. 2,7-Diethynyl-4-nitro-9*H*-fluorene (50). 4-Nitro-2,7-bis-trimethylsilanylethynyl-9*H*-fluorene (**49**) (0.700 g, 1.73 mmol), potassium carbonate (0.954 g, 6.90 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were used following the general deprotection method described earlier to afford the desired product (0.418 g, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.82 (m, 1H), 7.69 (m, 1H), 7.52 (m, 1H), 3.96 (s, 2H), 3.22 (s, 1H), 3.17 (s, 1H).

5.4.48. Thioacetic acid *S*-{4-[7-(4-acetylsulfanyl-phenylethynyl)-5-nitro-9*H*-fluoren-2-ylethynyl]-phenyl} ester (51). 2,7-Diethynyl-4-nitro-9*H*-fluorene (**50**) (0.418 g, 1.60 mmol), bis(dibenzylideneacetone)palladium(0) (0.046 g, 0.080 mmol), copper(I) iodide (0.030 g, 0.160 mmol), triphenylphosphine (0.084 g, 0.320 mmol), THF (65 mL), DIEA (1.1 mL, 6.4 mmol), and 4-(thioacetyl)iodobenzene (**7**) (0.934 g, 3.36 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 17 h. Column chromatography (silica gel using 5:1 CH_2Cl_2/hexanes; R_f=0.61) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as a yellow solid (0.402 g, 45% yield): mp 197–200°C. IR (KBr) 1708.2, 1526.7, 1488.8, 1354.1, 1287.8, 1119.0, 946.4, 829.2, 608.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.83 (d, J=1.4 Hz, 1H), 7.69 (m, 1H), 7.54 (m, 5H), 7.39 (m, 4H), 3.95 (s, 2H), 2.43 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 193.6, 147.2, 145.3, 145.0, 137.3, 134.7, 134.7, 134.2, 132.7, 132.6, 132.3, 131.5, 129.4, 128.8, 128.3, 126.9, 125.3, 124.6, 123.9, 123.3, 122.5, 91.7, 91.4, 90.9, 89.3, 37.1, 30.8, 30.7. HRMS calcd for $C_{33}H_{21}NO_4S_2$: 559.091203. Found: 559.091932 (Error=1.3 ppm).

5.4.49. 2-Ethynyl-4-nitro-7-phenylethynyl-9*H*-fluorene (52). 2,7-Dibromo-4-nitro-9*H*-fluorene (**48**) (1.00 g, 2.70 mmol) was coupled with TMSA (0.42 mL, 3.0 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.270 mmol), THF (30 mL), and DIEA (1.90 mL, 10.8 mmol) (the tube was cooled to 0°C before addition of TMSA). The reaction was allowed to warm to room temperature and stirred for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/CH_2Cl_2 as eluent; R_f=0.45) afforded the impure intermediate (0.849 g, ~57% by NMR) that was taken onto the next coupling following the Pd/Cu protocol. Bis(triphenylphosphine)-palladium(II) dichloride (0.077 g, 0.110 mmol), copper(I)

iodide (0.042 g, 0.219 mmol), THF (30 mL), and DIEA (1.53 mL, 8.76 mmol) and phenylacetylene (0.48 mL, 4.4 mL) were used with the crude material. The reaction was placed in a 55°C oil bath and stirred for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/CH_2Cl_2 as eluent; R_f=0.40) afforded the impure intermediate (0.453 g, ~90% by NMR) that was taken onto the step. Potassium carbonate (0.611 g, 4.42 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were added following the general deprotection method described earlier to afford the slightly impure (~95 % purity by NMR) product (0.373 g, ~41% yield over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2H), 7.77 (d, J=1.0 Hz, 1H), 7.67 (m, 1H), 7.52 (m, 4H), 7.34 (m, 4H), 3.91 (s, 2H), 3.21 (s, 1H).

5.4.50. Thioacetic acid *S*-[4-(4-nitro-7-phenylethynyl-9*H*-fluoren-2-ylethynyl)-phenyl] ester (53). 2-Ethynyl-4-nitro-7-phenylethynyl-9*H*-fluorene (**52**) (0.373 g, 1.11 mmol), bis(dibenzylideneacetone)palladium(0) (0.032 g, 0.055 mmol), copper(I) iodide (0.021 g, 0.111 mmol), triphenylphosphine (0.058 g, 0.220 mmol), THF (20 mL), DIEA (0.77 mL, 4.42 mmol), and 4-(thioacetyl)iodobenzene (**7**) (0.338 g, 1.22 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 1:1 CH_2Cl_2/hexanes) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as a yellow solid [0.297 g, ~55% yield (23% over 4 steps)]: mp 180–183°C. IR (KBr) 1713.9, 1544.6, 1516.6, 1490.7, 1346.4, 1289.3, 1117.0, 944.8, 824.0, 752.5, 689.8, 609.1, 537.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.87 (d, J=0.90 Hz, 1H), 7.73 (s, 1H), 7.56 (m, 5H), 7.42 (m, 2H), 7.37 (m, 3H), 4.00 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 147.2, 145.3, 145.0, 137.1, 134.7, 134.3, 132.7, 132.3, 132.1, 131.4, 129.4, 129.0, 128.8, 128.2, 126.9, 125.3, 124.4, 124.0, 123.4, 122.4, 91.7, 91.6, 89.8, 89.4, 37.1, 30.8. HRMS calcd for $C_{31}H_{19}NO_3S$: 485.108566. Found: 485.108900 (Error=0.69 ppm).

5.4.51. 7-Ethynyl-4-nitro-2-phenylethynyl-9*H*-fluorene (54). 2,7-Dibromo-4-nitro-9*H*-fluorene (**48**) (5.00 g, 13.5 mmol) was coupled with phenylacetylene (1.56 mL, 14.2 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.190 g, 0.27 mmol), copper(I) iodide (0.103 g, 0.54 mmol), THF (70 mL), and DIEA (9.4 mL, 54 mmol). The reaction was stirred at room temperature for 14 h at which point TMSA (2.86 mL, 20.2 mmol) was added. The tube was placed in a 55°C oil bath for 6 h. After workup, the reaction was found not to be complete. Therefore, the crude material was reacted with bis(triphenylphosphine)palladium(II) dichloride (0.095 g, 0.135 mmol), copper(I) iodide (0.051 g, 0.27 mmol), THF (70 mL), and DIEA (9.4 mL, 54 mmol). The tube was placed in a 60°C oil bath for 1 d. Flash column chromatography (silica gel using 3:1 hexanes/CH_2Cl_2 as eluent; R_f=0.43) afforded the impure intermediate (2.25 g, ~94% by NMR) that was taken onto the next step. Potassium carbonate (3.04 g, 22 mmol), methanol (100 mL), and CH_2Cl_2 (100 mL) were added following the general deprotection method described earlier to afford the slightly impure (~93 % purity by NMR) product (1.75 g, ~41% yield over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 1H), 8.02 (d, J=8.3 Hz, 1H), 7.87 (m, 1H), 7.69 (m, 1H), 7.54 (m, 3H), 7.37 (m, 3H), 3.98 (s, 2H), 3.18 (s, 1H).

5.4.52. Thioacetic acid *S*-[4-(5-nitro-7-phenylethynyl-9*H*-fluoren-2-ylethynyl)-phenyl] ester (55). 7-Ethynyl-4-nitro-2-phenylethynyl-9*H*-fluorene (**54**) (0.875 g, 2.59 mmol), bis(dibenzylideneacetone)palladium(0) (0.074 g, 0.13 mmol), copper(I) iodide (0.049 g, 0.26 mmol), triphenylphosphine (0.136 g, 0.520 mmol), THF (35 mL), DIEA (1.80 mL, 10.4 mmol), and 4-(thioacetyl)iodobenzene (**7**) (0.792 g, 2.85 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 2:1 CH_2Cl_2/hexanes as eluent; R_f=0.60) followed by precipitation from CH_2Cl_2/hexanes afforded the desired product as a yellow solid [0.841 g, ~67% yield (25% over 4 steps)]: mp 192–195°C. IR (KBr) 3042.1, 2202.1, 1705.1, 1520.1, 1491.6, 1350.2, 1287.1, 1111.7, 944.4, 827.4, 757.8, 691.6, 614.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.86 (m, 1H), 7.72 (m, 1H), 7.55 (m, 5H), 7.37 (m, 5H), 3.98 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 147.2, 145.4, 145.0, 137.5, 134.7, 133.9, 132.6, 132.2, 132.2, 131.5, 129.4, 128.9, 128.7, 128.3, 126.9, 125.3, 124.7, 123.9, 122.9, 122.8, 92.6, 91.5, 90.8, 87.8, 37.1, 30.7. HRMS calcd for $C_{31}H_{19}NO_3S$: 485.108566. Found: 485.108470 (Error=0.20 ppm).

5.4.53. *N*-[4-(5-Nitro-7-phenylethynyl-9*H*-fluoren-2-ylethynyl)-phenyl]-formamide (56). 7-Ethynyl-4-nitro-2-phenylethynyl-9*H*-fluorene (**54**) (0.875 g, ~2.59 mmol) was coupled with *N*-(4-iodo-phenyl)-formamide (**9**) (0.704 g, 2.85 mmol) following the Pd/Cu protocol using bis(dibenzylideneacetone) palladium(0) (0.074 g, 0.129 mmol), copper(I) iodide (0.049 g, 0.26 mmol), triphenylphosphine (0.136 g, 0.518 mmol), DIEA (1.80 mL, 10.3 mmol), and THF (35 mL). The tube was placed in a 55°C oil bath for 3 h. Column chromatography (silica gel using 3:1 CH_2Cl_2/ethyl acetate; R_f=0.35) afforded the impure product (1.07 g) which was taken directly onto the next step. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 0.9H), 10.35 (d, J=10.7 Hz, 0.3H), 8.90 (d, J=10.8 Hz, 0.3H), 8.32 (d, J=1.5 Hz, 1H), 8.11 (s, 1H), 8.07 (s, 1H), 7.86–7.81 (m, 2.3H), 7.73–7.45 (m, 13H), 7.26 (d, J=8.4 Hz, 0.7H).

5.4.54. 7-(4-Isocyano-phenylethynyl)-4-nitro-2-phenylethynyl-9*H*-fluorene (57). To a 500 mL round bottom flask was added *N*-[4-(5-nitro-7-phenylethynyl-9*H*-fluoren-2-ylethynyl)-phenyl]-formamide (**56**) (1.07 g, ~2.30 mmol). Air was removed and N_2 backfilled (3×). CH_2Cl_2 (250 mL) and triethylamine (50 mL) was added and the flask was cooled to 0°C. Triphosgene (0.434 g, 1.61 mmol) was then added. After 3 h the solution was at room temperature and starting material remained by TLC. An additional 0.124 g (0.46 mmol) of triphosgene was added. After 15 min (3.25 h total time), the reaction was complete by TLC. The mixture was washed with water and CH_2Cl_2. Column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent; R_f=0.39) followed by precipitation from CH_2Cl_2/hexanes afforded the product (0.356 g, 31% yield over 2 steps): mp 210–225°C (decomp.). IR (KBr) 3068.0, 2119.2, 1519.9, 1504.2, 1360.8, 1287.6, 838.3, 752.8, 686.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.83 (s, 1H), 7.68 (s, 1H), 7.53 (m, 5H), 7.36 (m, 5H), 3.96

(s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 147.2, 145.4, 145.0, 137.7, 133.7, 133.0, 132.2, 132.2, 131.5, 129.4, 128.9, 128.3, 126.9, 126.9, 125.3, 124.9, 123.31, 123.11, 122.73, 92.67, 92.56, 89.79, 87.74, 37.07. HRMS calcd for $C_{30}H_{16}N_2O_2$: 436.121178. Found: 436.121833 (Error=1.5 ppm).

5.4.55. 2,7-Dibromo-fluoren-9-one (58).[26] 2,7-Dibromofluorene (**47**) (10.0 g, 30.7 mmol) was added to a 500 mL round bottom flask equipped with a stir bar along with CH_2Cl_2 (400 mL). *t*-Butyl hydroperoxide (20.6 mL, 215 mmol) and catalytic chromium(III) oxide (0.153 g, 1.53 mmol) were then added. The solution was stirred at ambient temperature for 1 d, at which point starting material remained. The solution was then heated to reflux for 19 h. After cooling to ambient temperature, the solution was filtered through alumina. ^{1}H NMR showed approximately 50% conversion. The mixture was re-subjected to the reaction conditions with 0.306 g (3.07 mmol) of chromium(III) oxide and heated to reflux for 20 h. The material was filtered through alumina (^{1}H NMR showed approximately 90% product). The product was then recrystallized from ethanol/toluene to afford the pure product (8.65 g, 83% yield): mp 205–209°C (lit. mp 205–207°C).[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J=1.8 Hz, 2H), 7.61 (dd, J=7.9, 1.9 Hz, 2H), 7.37 (d, J=7.9 Hz, 2H).

5.4.56. 2,7-Bis-trimethylsilanylethynyl-fluoren-9-one (59).[27] 2,7-Dibromo-9-oxo-fluorene (**58**) (0.753 g, 2.21 mmol) was coupled with TMSA (0.69 mL, 4.9 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.078 g, 0.110 mmol), copper(I) iodide (0.042 g, 0.22 mmol), THF (20 mL), and DIEA (2.30 mL, 13.3 mmol). The tube was capped and stirred at 50°C for 15 h. Flash column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent; R_f=0.47) afforded the desired product (0.480 g, 58% yield): mp 164–168°C. IR (KBr) 2958.4, 2898.7, 2154.6, 1715.0, 1603.5, 1463.6, 1249.5, 859.1, 758.7, 644.7, 535.7 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J=1.5, 0.7 Hz, 2H), 7.56 (dd, J=7.7, 1.5 Hz, 2H), 7.43 (dd, J=7.7, 0.7 Hz, 2H), 0.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 143.8, 138.6, 134.7, 128.3, 124.8, 120.9, 104.3, 97.1, 0.3.

5.4.57. 2,7-Diethynyl-fluoren-9-one (60).[27] 2,7-Bis-trimethylsilanylethynyl-fluoren-9-one (**59**) (0.480 g, 1.28 mmol), potassium carbonate (0.709 g, 5.13 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were used following the general deprotection method described earlier to afford the desired product (0.285 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 2H), 7.61 (dd, J=7.7, 1.5 Hz, 2H), 7.48 (d, J=7.8 Hz, 2H), 3.17 (s, 2H).

5.4.58. Thioacetic acid *S*-{4-[7-(4-acetylsulfanyl-phenylethynyl)-9-oxo-9*H*-fluoren-2-ylethynyl]-phenyl} ester (61). 2,7-Diethynyl-fluorenone (**60**) (0.285 g, 1.24 mmol), bis(dibenzylideneacetone)palladium(0) (0.036 g, 0.062 mmol), copper(I) iodide (0.024 g, 0.124 mmol), triphenylphosphine (0.065 g, 0.248 mmol), THF (25 mL), DIEA (1.30 mL, 7.44 mmol), and 4-(thioacetyl)iodobenzene (**7**) (0.690 g, 2.48 mmol) were used following the general procedure for couplings. The tube was placed in a 50°C oil bath for 4 h. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.47) afforded the desired product as a yellow solid (0.370 g, 56% yield): mp 239–241°C. IR (KBr) 1725.8, 1702.5, 1600.3, 1490.4, 1101.9, 957.3, 829.8, 785.3, 618.8, 526.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=0.8 Hz, 2H), 7.65 (dd, J=7.9, 1.4 Hz, 2H), 7.53 (m, 6H), 7.40 (d, J=8.4 Hz, 2H), 2.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 192.5, 143.8, 138.3, 134.9, 134.7, 132.6, 129.0, 127.9, 124.6, 124.4, 121.1, 91.1, 90.5, 30.7. HRMS calcd for $C_{33}H_{20}O_3S_2$: 528.085390. Found: 528.085952 (Error=1.1 ppm).

5.4.59. 2,7-Dibromo-4-nitro-fluoren-9-one (62).[24] 2,7-Dibromo-4-nitro-9*H*-fluorene (**48**) (1.00 g, 2.70 mmol) and CH_2Cl_2 (60 mL) were added to a 100 mL round bottom flask equipped with a stir bar. Chromium(III) oxide (0.013 g, 0.135 mmol) and *t*-butyl hydroperoxide (1.80 mL, 18.9 mmol) were then added and the solution was stirred at ambient temperature for 1 d (red solution). The solution was then heated to reflux for 19 h (yellow solution). After cooling to ambient temperature, the mixture was filtered through alumina. Column chromatography (silica gel using 1:1 CH_2Cl_2/hexanes as eluent; R_f=0.51) afforded the desired product as a yellow solid (0.637 g, ~95% pure). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J=1.8 Hz, 1H), 8.02 (d, J=1.9 Hz, 1H), 7.91 (d, J=8.3 Hz, 1H), 7.88 (d, J=2.0 Hz, 1H), 7.71 (dd, J=8.3, 2.0 Hz, 1H).

5.4.60. 4-Nitro-2,7-bis-trimethylsilanylethynyl-fluoren-9-one (63). 2,7-Dibromo-4-nitro-fluorenone (**62**) (0.637 g, 1.65 mmol) was coupled with TMSA (0.51 mL, 3.6 mmol) following the Pd/Cu protocol using bis(triphenylphosphine)palladium(II) dichloride (0.058 g, 0.083 mmol), copper(I) iodide (0.031 g, 0.165 mmol), THF (25 mL), and triethylamine (5 mL). The tube was capped and stirred at ambient temperature for 5 h. Flash column chromatography (silica gel using 2:1 hexanes/CH_2Cl_2 as eluent; R_f=0.61) afforded the desired product (0.475 g, 42% yield over 2 steps): mp 234–235°C. IR (KBr) 2958.1, 2903.8, 2156.0, 1732.1, 1557.9, 1531.4, 1453.2, 1356.3, 1249.2, 845.2, 767.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J=1.5 Hz, 1H), 7.93 (m, 2H), 7.81 (d, J=1.6 Hz, 1H), 7.62 (dd, J=8.1, 1.7 Hz, 1H), 0.26 (s, 9), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 144.8, 139.6, 139.2, 137.1, 136.0, 134.9, 133.3, 131.6, 128.4, 126.8, 126.4, 126.0, 103.6, 101.6, 100.8, 99.2, 0.2, 0.1. HRMS calcd for $C_{23}H_{23}NO_3Si_2$: 417.121651. Found: 417.121826 (Error=0.42 ppm).

5.4.61. 2,7-Diethynyl-4-nitro-fluoren-9-one (64). 4-Nitro-2,7-bis-trimethylsilanylethynyl-fluoren-9-one (**63**) (0.450 g, 1.07 mmol), potassium carbonate (0.887 g, 6.42 mmol), methanol (50 mL), and CH_2Cl_2 (50 mL) were used following the general deprotection method described earlier to afford the desired product (0.290 g) which was taken directly onto the next step with no further purification.

5.4.62. Thioacetic acid *S*-{4-[7-(4-acetylsulfanyl-phenylethynyl)-5-nitro-9-oxo-9*H*-fluoren-2ylethynyl]-phenyl} ester (65). 2,7-Diethynyl-4-nitro-fluorenone (**64**) (0.290 g, 1.05 mmol), bis(dibenzylideneacetone)palladium(0) (0.030 g, 0.053 mmol), copper(I) iodide (0.020 g, 0.105 mmol), triphenylphosphine (0.055 g, 0.21 mmol), THF (25 mL), DIEA (1.1 mL, 6.3 mmol), and 4-(thioacetyl)iodobenzene

(**7**) (0.613 g, 2.21 mmol) were used following the general procedure for couplings. The tube was placed in a 55°C oil bath for 18 h. Column chromatography (silica gel using CH_2Cl_2 as eluent; R_f=0.63), followed by precipitation form CH_2Cl_2/hexanes (to remove dba) afforded the desired product as an orange solid (0.372 g, 60% yield over 2 steps): mp 234–236°C. IR (KBr) 2202.1, 1724.8, 1557.4, 1528.2, 1492.1, 1454.4, 1354.4, 1235.5, 1113.1, 1090.7, 937.0, 822.0, 602.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J=1.5 Hz, 1H), 7.97 (m, 2H), 7.84 (d, J=1.2 Hz, 1H), 7.67 (dd, J=8.1, 1.6 Hz, 1H), 7.55–7.52 (m, 4H), 7.42–7.38 (m, 4H), 2.43 (s, 3H), 2.42 (s, 3H).HHH ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 193.4, 189.9, 144.9, 139.6, 138.9, 137.2, 135.1, 134.7, 134.7, 133.0, 132.8, 132.7, 131.2, 130.0, 129.5, 128.0, 126.6, 126.6, 125.8, 123.9, 123.3, 93.8, 92.8, 89.9, 88.1, 30.8, 30.8. HRMS calcd for $C_{33}H_{19}NO_5S_2$: 573.070468. Found: 573.071403 (Error=1.6 ppm).

5.4.63. 2,3′-Dinitro-4,4′-bis-phenylethynyl-benzene (66). 4,4′-Dibromo-2,3′-dinitrobiphenyl (**3**) (0.402 g, 1.00 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.050 mmol), copper(I) iodide (0.019 g, 0.10 mmol), triphenylphosphine (0.033 g, 0.125 mmol), THF (10 mL), DIEA (0.70 mL, 4.0 mmol), and phenylacetylene (0.33 mL, 3.0 mmol) were used following the general procedure for couplings. The tube was capped and the solution heated in a 70°C oil bath for 1 d. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product (0.355 g, 80% yield): mp 144–147°C. IR (KBr) 3080.9, 2847.8, 2213.0, 1542.0, 1521.4, 1440.9, 1341.0, 1279.1, 1140.0, 1071.9, 889.7, 837.0, 761.6, 689.9, 529.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=1.6 Hz, 1H), 8.07 (d, J=1.8 Hz, 1H), 7.79 (dd, J=8.0, 1.6 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.60 (m, 2H), 7.55 (m, 2H), 7.50 (dd, J=8.0, 1.9 Hz, 1H), 7.44 (d, J=7.9 Hz, 1H), 7.38 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.8, 138.1, 136.0, 135.2, 133.3, 132.7, 132.5, 132.3, 129.9, 129.7, 129.0, 128.9, 128.0, 125.9, 124.8, 122.7, 122.4, 119.2, 99.1, 93.8, 86.8, 85.0. HRMS calcd for $C_{28}H_{16}N_2O_4$: 444.1110. Found: 444.1110 (Error=0.03 ppm).

5.4.64. 2,2′-Dinitro-4,4′-bis-phenylethynyl-benzene (67). 4,4′-Dibromo-2,2′-dinitrobiphenyl (**17**) (1.00 g, 2.49 mmol), bis(dibenzylideneacetone)palladium(0) (0.043 g, 0.075 mmol), copper(I) iodide (0.014 g, 0.075 mmol), triphenylphosphine (0.050 g, 0.19 mmol), THF (15 mL), DIEA (1.73 mL, 9.96 mmol), and phenylacetylene (0.68 mL, 6.2 mmol) were used following the general procedure for couplings. The tube was capped and the solution was heated in a 50°C oil bath for 2 d. Flash column chromatography (silica gel using 1:1 hexanes/CH_2Cl_2 as eluent) afforded the desired product (0.955 g, 86% yield): mp 234–236°C. IR (KBr) 3078.2, 2212.5, 1595.1, 1546.5, 1531.6, 1490.2, 1441.7, 1350.1, 1070.8, 898.7, 839.6, 827.4, 765.1, 692.8, 530.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J=1.6 Hz, 2H), 7.79 (dd, J=7.9, 1.7 Hz, 2H), 7.56 (m, 4H), 7.38 (m, 6H), 7.27 (d, J=7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 136.4, 133.5, 132.3, 131.4, 129.6, 129.0, 128.1, 125.7, 122.5, 93.3, 86.9. HRMS calcd for $C_{28}H_{16}N_2O_4$: 444.1110. Found: 444.1113 (Error=0.73 ppm).

Acknowledgements

We thank the Defense Advanced Research Projects Agency (DARPA) administered by the Office of Naval Research (ONR), and the Air Force Office of Scientific Research (AFOSR F49620-01-1-0364) for financial support of this work. We thank Dr I. Chester of FAR Research Inc. for trimethylsilylacetylene and Jake Ciszek for obtaining the crystal of **53** and the X-ray analysis.

References

1. Service, R. F. *Science* **2001**, *294*, 2442–2443.
2. (a) Montemerlo, M. S.; Love, J. C.; Opiteck, G. J.; Goldhaber-Gordon, D.; Ellenbogen, J. C. *Technologies and Designs for Electronic Nanocomputers*; MITRE Corporation, 1996. (b) The International Technology Roadmap for Semiconductors (ITRS) can be found at the URl **1** and the nitro functionalized **2** demonstrated the NDR effect.
3. Tour, J. M. *Acc. Chem. Res.* **2000**, 791–804.
4. Tour, J. M.; Kozaki, M.; Seminario, J. *J. Am. Chem. Soc.* **1998**, 8486–8493.
5. Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L., II.; Tour, J. M. *Appl. Phys. Lett.* **1997**, 611–613.
6. Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, 1550–1552.
7. Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Appl. Phys. Lett.* **2000**, 1224–1226.
8. Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Mater. Res. Soc. Symp. Proc.* **2001**, *5582*, H321–H325.
9. Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, 3015–3020.
10. Price, D. W.; Dirk, S. M.; Rawlett, A. M.; Chen, J.; Wang, W.; Reed, M. A.; Zacarias, A. G.; Seminario, J. M.; Tour, J. M. *Mater. Res. Soc. Symp. Proc.* **2001**, *660*, JJ941/D741–JJ949/D749.
11. Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2001**, *78*, 3735–3737.
12. Mark Reed, Yale University, personal communication.
13. (a) Shaw, F. R.; Turner, E. E. *J. Chem. Soc.* **1932**, 285–297. (b) Shaw, F. R.; Turner, E. E. *J. Chem. Soc.* **1932**, 509–513.
14. Rosen, G. M.; Tsai, P.; Barth, E. D.; Dorey, G.; Casara, P.; Spedding, M.; Halpern, H. J. *J. Org. Chem.* **2000**, *65*, 4460–4463.
15. Quintanilla-Licea, R.; Colunga-Valladares, J. F.; Caballero-Quintero, A.; Rodriguez-Padilla, C.; Tamez-Guerra, R.; Gómez-Flores, R.; Waksman, N. *Molecules* **2002**, *7*, 662–673, http://www.mdpi.org.
16. Yamato, T.; Hideshima, C.; Suehiro, K.; Tashiro, M.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1991**, *56*, 6248–6250.
17. Dirk, S. M.; Mickelson, E. T.; Henderson, J. C.; Tour, J. M. *Org. Lett.* **2000**, *2*, 3405–3406.
18. Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376–1387.
19. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467–4470.
20. Wilson, J. G.; Hunt, F. C.; Aust, *J. Chem.* **1983**, *36*, 2317–2325.
21. 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. *Chem. Eur. J.* **2001**, *7*, 5118–5134.
22. Stille, J. K. *Angew. Chem. Int. Ed.* **1986**, *25*, 508–524.
23. Ranger, M.; Leclerc, M.; Can, *J. Chem.* **1998**, *76*, 1571–1577.
24. Pan, H.-L.; Fletcher, T. L. *J. Med. Chem.* **1965**, *8*, 491–497.
25. Muzart, J. *Tetrahedron Lett.* **1987**, *28*, 2131–2132.
26. Bergmann, E.; Hervey, J. *Chem. Ber.* **1929**, *62*, 803–916.
27. Lewis, J.; Raithby, P. R.; Wong, W.-Y. *J. Organomet. Chem.* **1998**, *556*, 219–228.
28. Reed, M.A., Price, D.W., Tour, J.M., unpublished preliminary data.
29. Wu, J.; Chi, C.; Wang, X.; Li, J.; Zhao, X.; Wang, F. *Synth. Commun.* **2000**, *30*, 4293–4298.
30. Krishnamurthy, S. *Tetrahedron Lett.* **1982**, *23*, 3315–3318.
31. Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.
32. Brenans, P. *Bull. Soc. Chim. Fr.* **1902**, *3*, 965.
33. Borowitz, I. J.; Anschel, M.; Readio, P. D. *J. Org. Chem.* **1971**, *36*, 553–560.
34. Sprinzak, Y. *J. Am. Chem. Soc* **1958**, *80*, 5449–5452.