

# Synthesis of terphenyl oligomers as molecular electronic device candidates

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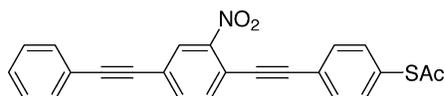
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**Abstract**—Six functionalized bis(phenylene ethynylene)-*p,p*-terphenyls (BPETs) have been synthesized as potential molecular electronic devices. The molecules containing mono- and dinitro terphenyl cores, were rationally designed based on the electronic properties recently found in oligo(phenylene ethynylene)s (OPEs). From our understanding of the conductance properties in OPEs, improvement of electronic properties may be possible by using BPETs due to a higher rotational barrier between the central aromatic rings of the compounds prepared here. BPETs cores were functionalized with nitro groups and with different metallic adhesion moieties (alligator clips) to provide new compounds for testing in the nanopore and planar testbed structures.  
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## 1. Introduction

In the field of molecular electronics, several groups,<sup>1</sup> including our own,<sup>2</sup> have been pursuing the ultimate miniaturization of electronic components, synthesizing diverse organic molecules that can be used as electronic devices. Oligo(phenylene ethynylene)s (OPEs) have been synthesized and tested by new electronic screening methods,<sup>3</sup> engineered nanoscale arrays,<sup>4</sup> and lithographic motifs;<sup>5</sup> thereby recording non-linear conductive properties over metallic<sup>6</sup> and semiconductor layers.<sup>7</sup> Our approach capitalizes on the conformational diversity and functionality of such molecules.<sup>8</sup> Chemical functionalization of OPEs with nitro groups (Fig. 1) has yielded switching properties that were not seen in the unfunctionalized systems.<sup>9–11</sup> The presence of redox groups in the molecule might be responsible for a negative differential resistance (NDR) at room temperature<sup>12</sup> and programmability as memory devices.<sup>13</sup>



**Figure 1.** The mononitro OPE that has exhibited NDR in several testbeds.

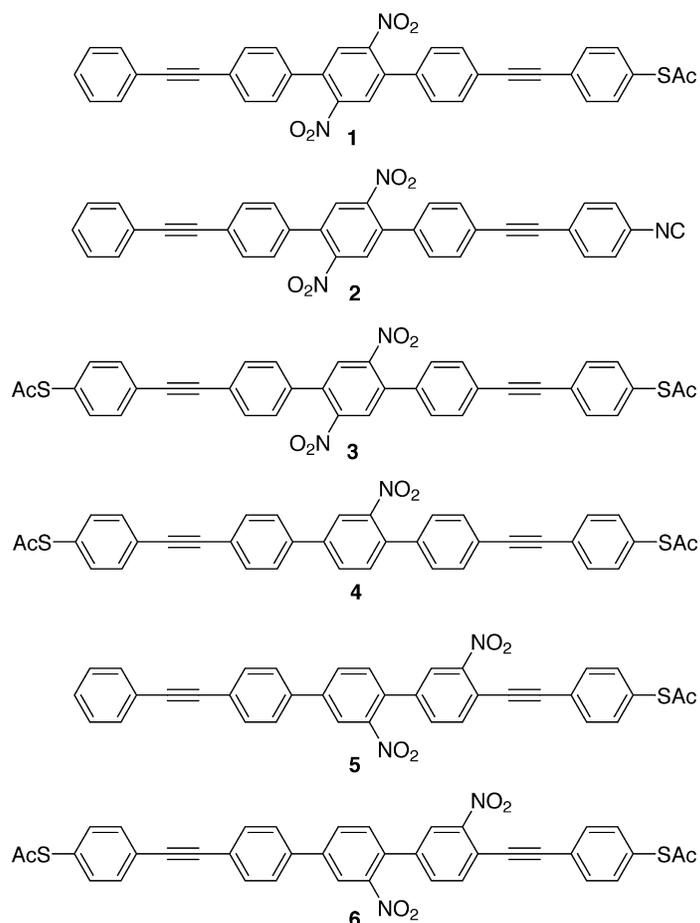
Several recent studies suggested the conformational characteristics and nitro functionalization are the main sources of the

electronic switching characteristics of the molecules.<sup>14,15</sup> Theoretical works have complemented the experimental work with assorted insights,<sup>16,17</sup> suggesting on one hand that high internal rotational energy barriers in linear conjugated molecules are the main causes for the switching effects.<sup>18</sup> On the other hand, the switching phenomenon has been attributed to temporal dipolar moments as the result of electron charges that are facilitated by redox groups on the molecule.<sup>14,15,19</sup> However, newer mechanisms are suggesting that the NDR is not molecularly-inherent, rather the switching is based upon the metal-molecule contact junctions.<sup>14,20</sup>

In this context, terphenyl molecules have recently shown unusual electrical properties,<sup>21</sup> and a high dependence on conformation for electronic conduction.<sup>22</sup> Moreover, terphenyls have shown temperature and solvent effects upon the electronic flow through the systems,<sup>23</sup> high thermal and photo-stability,<sup>24,25</sup> while presenting long-range ordered layers on gold<sup>26</sup> and silver substrates.<sup>27</sup> It is also known that high rigidity and extended  $\pi$ -conjugation of terphenyl thiols result in dense and stable monolayer structures that show lower tunneling barriers when compared to other molecular conjugated structures.<sup>28,29</sup> Finally, their strong dependence on intermolecular forces, conformation, solvent, effective conjugation and geometrical modifications make terphenyl oligomers attractive synthetic targets for further electronic testing.<sup>30</sup> These facts have motivated us to pursue the synthesis of new bis(phenylene ethynylene)-*p,p*-terphenyls (BPETs) as molecular device candidates (Fig. 2). The syntheses are presented so as to focus on the commonality of intermediates en route to the targets.

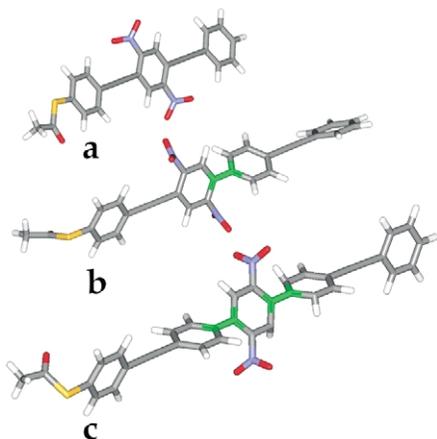
**Keywords:** Terphenyl; Molecular electronic; Conformational Energy.

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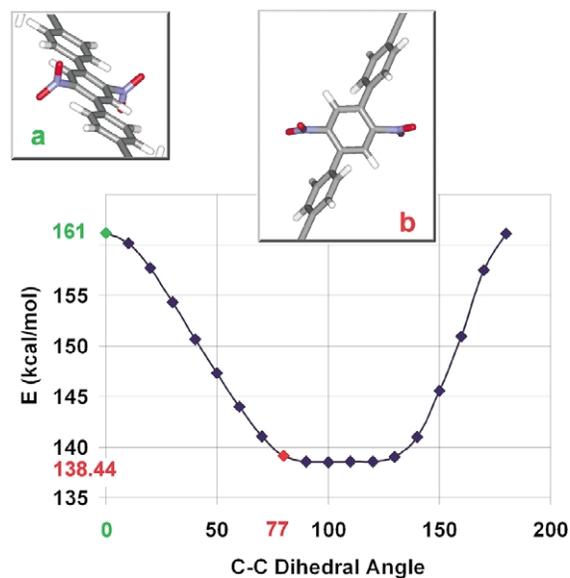
**Figure 2.** Synthetic targets presented in this work.

BPETs are expected to have a more rigid molecular core with lower conformational freedom, compared with OPEs (Fig. 3). Limited rotations of the C–C bonds between central aromatic rings of the molecule would result in geometrical restrictions. While the OPE pictured in Figure 1 shows no substantial increment in energy from the rotation of the central ring,<sup>16</sup> a biphenyl OPE and terphenyl OPE (Fig. 3(b) and (c), respectively) present significant rotational barriers relative to the OPE (Fig. 3(a)).



**Figure 3.** Conformers of different oligomers with (a) zero (b) one, and (c) two rotational barriers from C–C phenyl bonds, highlighted in green.

It is expected that the presence of more than one rotational barrier in the molecule would produce a clear difference between the two conformational states of the molecule: a high energy and a low energy conformation (Fig. 4).



**Figure 4.** Relative energies at different C–C dihedral angles of optimized structures of **3** by molecular mechanics.<sup>31</sup> Inset a shows the geometry of the central core when the dihedral angles equal zero (values in green). A local minimum shows the geometry of inset b, with a dihedral angle of ca. 77° (values in red).

A high energy conformation of a BPET like **3** would exhibit planar central rings, where overlapping of  $\pi$ -orbitals would impart full conjugation and electron transport to the nitro groups (Fig. 4, inset a). The low energy conformation requires the cancellation of this extended conjugation when the phenyl rings are non-planar and an electron might be more localized in the molecular orbital of one of the electron-withdrawing groups. This localization might have significant effects on the ability of the oligomer to operate as a molecular memory device with extended periods of electron retention, albeit with a larger barrier to electronic transport.

## 2. Synthesis

The syntheses<sup>32–41</sup> of BPETs start with the functionalization of the central cores. Scheme 1 shows the synthetic route to the nitroaniline precursor **11**.

Nitration of dibromobenzene gave the nitro intermediate **7**. Reduction with tin(II) chloride and subsequent protection of the resulting aniline **8** gave the acetamide **9** in high yield. A second nitration at the 4-position selectively provided **10**, and a final alkaline deprotection of the acetamide afforded the desired nitroaniline **11**.

The synthesis of **1** began by coupling commercially available 4-bromoiodobenzene with phenylacetylene at the

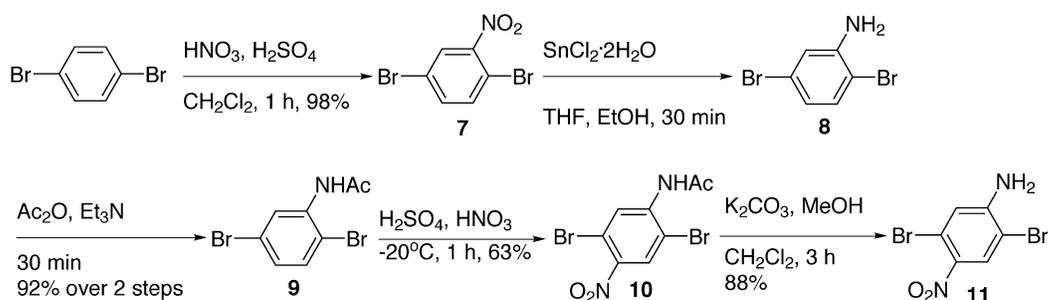
iodide position as shown in Scheme 2, although inseparable small amounts of the dicoupled byproduct were carried with **12** through the lithium–bromide exchange reaction and stannylation.

The synthesis of the biphenyl backbone is done by a Stille coupling reaction,<sup>42</sup> between the nitroaniline **11** and the stannane **13**. The coupling was chemoselective, undergoing reaction alpha to the more activating nitro group as we have seen in the past,<sup>37</sup> furnishing aniline **14**. The second nitro group for the central ring was introduced by oxidizing the amino group, using HOF generated in situ from water and fluorine,<sup>32</sup> giving **15**.

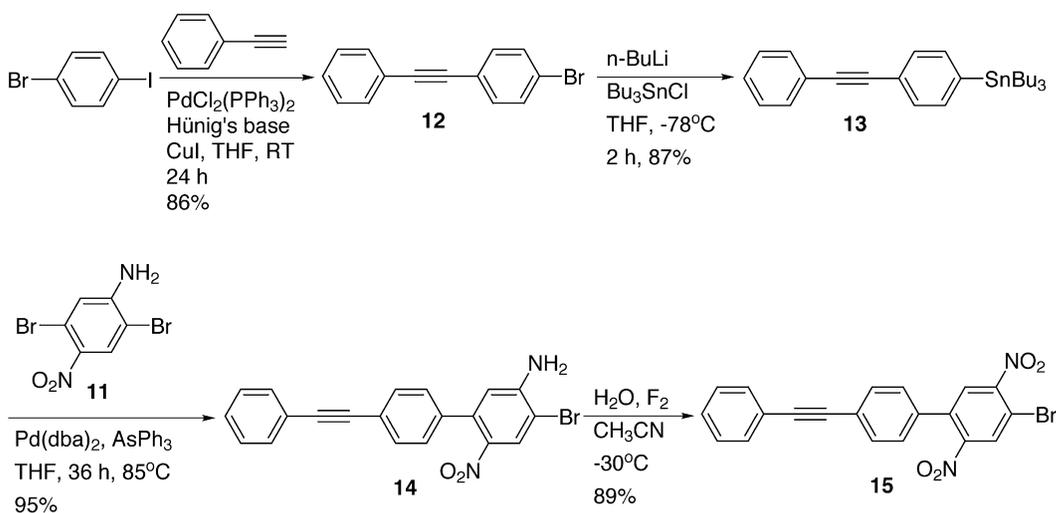
Scheme 3 shows the synthesis of the target BPET **1**.

4-Bromo-1-iodobenzene was selectively coupled with trimethylsilylacetylene (TMSA) to afford **16**, followed by a stannylation to **17**. Stille coupling between **15** and the stannane **17**, afforded **18** which was prepared for a final Sonogashira coupling.<sup>40</sup> 4-(Thioacetyl)iodobenzene **20**,<sup>33</sup> a protected thiol terminus for the metal-molecular junction (or alligator clip), was coupled with **19** to afford the target **1**.

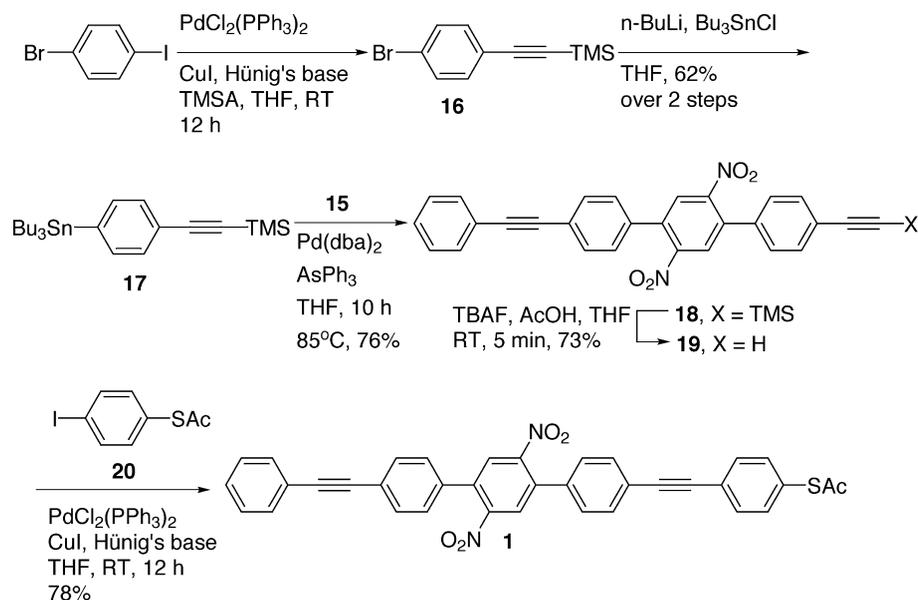
4-Iodoaniline was treated with ethyl formate to yield formamide **21**, a precursor of an isocyanide alligator clip. The formamide could be coupled with the same dinitro-terphenyl core, **19**, to afford **22** (Scheme 4). The low yield could be due to the low solubility of **22**, which is a common



Scheme 1.



Scheme 2.



Scheme 3.

feature of formamides. A final dehydration of **22** using the phosgene precursor, triphosgene,<sup>34</sup> afforded the desired BPET isonitrile **2**.

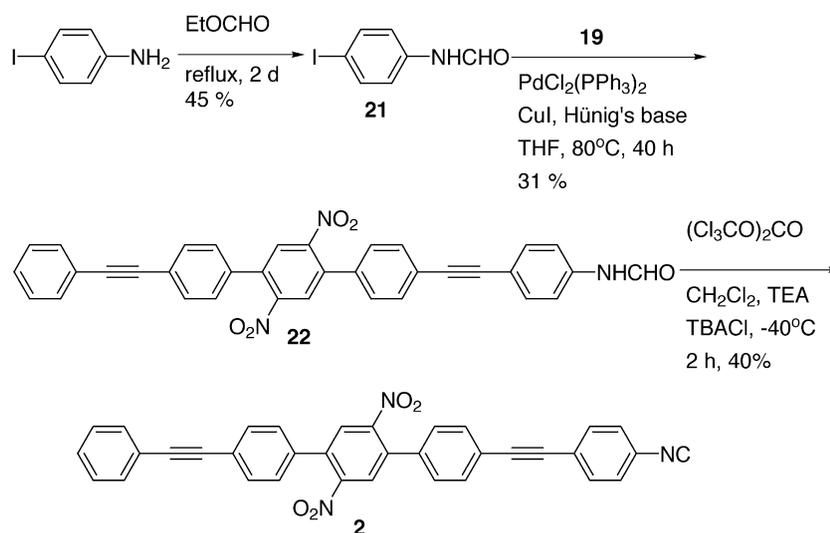
The convenient nitroaniline intermediate **11** was used in synthetic paths toward several other targets including the symmetric dinitro-terphenyls with alligator clips at both sides as illustrated in Scheme 5.

Oxidation of **11** by HOF provided the desired dinitro central precursor **23**. The stannane **17** was used for a double Stille coupling on both halides of **23**, in order to afford **24**. The high yield for this double coupling might indicate the high activation of the bromides toward oxidative addition by the two nitro groups. Bis-deprotection of **24** afforded **25** in low yield, probably due to the poor solubility and instability of bis-terminal alkynes of highly electron deficient systems, a phenomenon that we have consistently observed.<sup>37</sup> A final coupling with the protected-thiol alligator clip **20** yielded

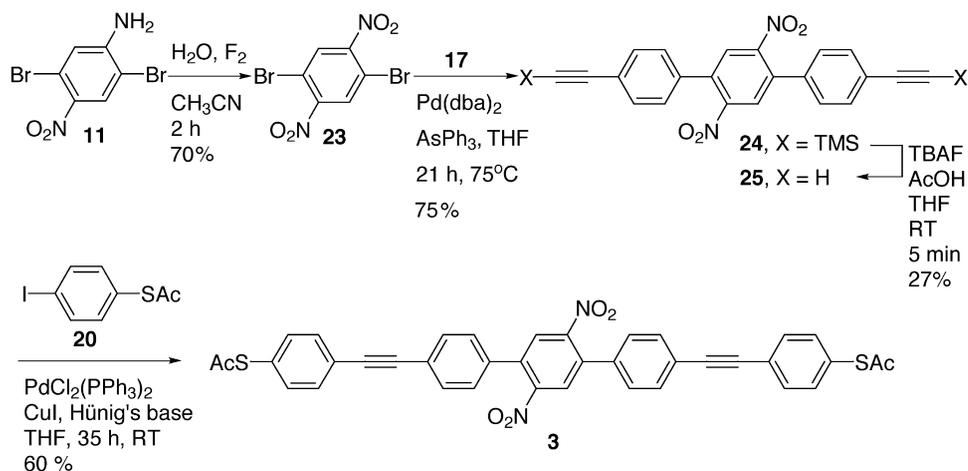
the desired symmetric BPET **3**. In the future, it may be advantageous to carry out an in situ TMS-removal and coupling between **20** and **25**, thereby obviating the need to isolate the unstable dialkyne **25**.<sup>35</sup>

Variation of functional groups, both number and location, can have a profound influence on the electronic properties of the oligomers.<sup>15,38</sup> Considering this, the mononitro BPET **4** was prepared using a protocol similar to that described above.

2-Nitroaniline was iodinated at the 4-position, according to a known procedure,<sup>36</sup> affording **26**, followed by diazotization and iodination to give **27** (Scheme 6). A Stille coupling to both iodides gave the mononitro terphenyl **28**, as well as mono-coupled byproducts. Note that if 2,5-dibromonitrobenzene (**7**) was used with **17** to form terphenyl intermediate **28**, the yield decreased to 56%, suggesting that the iodides on this compound are more reactive for Stille coupling than the bromides from compound **7** (Scheme 1).



Scheme 4.



Scheme 5.

Deprotection of both alkynes furnished **29** as the terphenyl intermediate. Once deprotected, both alkynes underwent Sonogashira coupling with the alligator clip **20** in order to give the desired mononitro-BPET **4**. Similar yields were found when Hünig's base was used instead of triethylamine (TEA).

In the synthesis of a dinitro BPET **5**, it was found that nitration of a starting biphenyl core conveniently permitted the exclusion of one carbon–carbon bond formation step in our route toward the construction of the terphenyl moiety; the nitro-functionalization occurred on two aromatic rings,<sup>37</sup> as illustrated in Scheme 7.

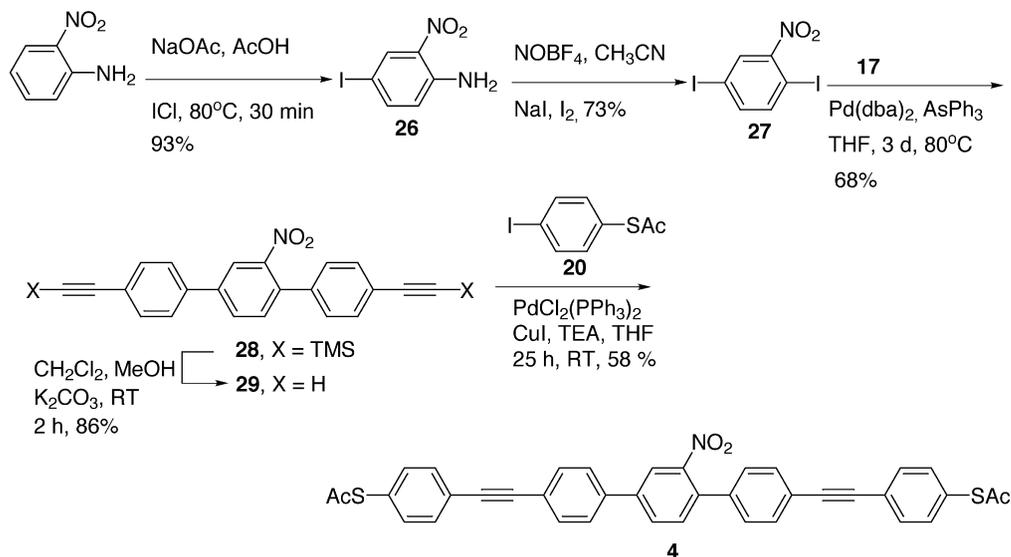
Initial nitric acid treatment of 4,4'-dibromobiphenyl in sulfuric acid gave the 2,3'-dinitrobiphenyl **30**, as the major product, separable from the 2,2'-dinitro isomer by crystallization.<sup>37</sup> TMSA coupled selectively to the bromide at the position *ortho* to the nitro group, yielding **31**. A Stille coupling using the previously synthesized stannane **13** gave a new dinitro terphenyl intermediate **32**. Alkaline deprotection yielded the free alkyne **33**, ready for a final coupling with alligator clip **20**, affording the desired unsymmetrical dinitro BPET **5**.

By using intermediate **31**, it was possible to construct a double functionalized unsymmetrical BPET, as shown in Scheme 8, by just changing the stannane from **13** to **17**.

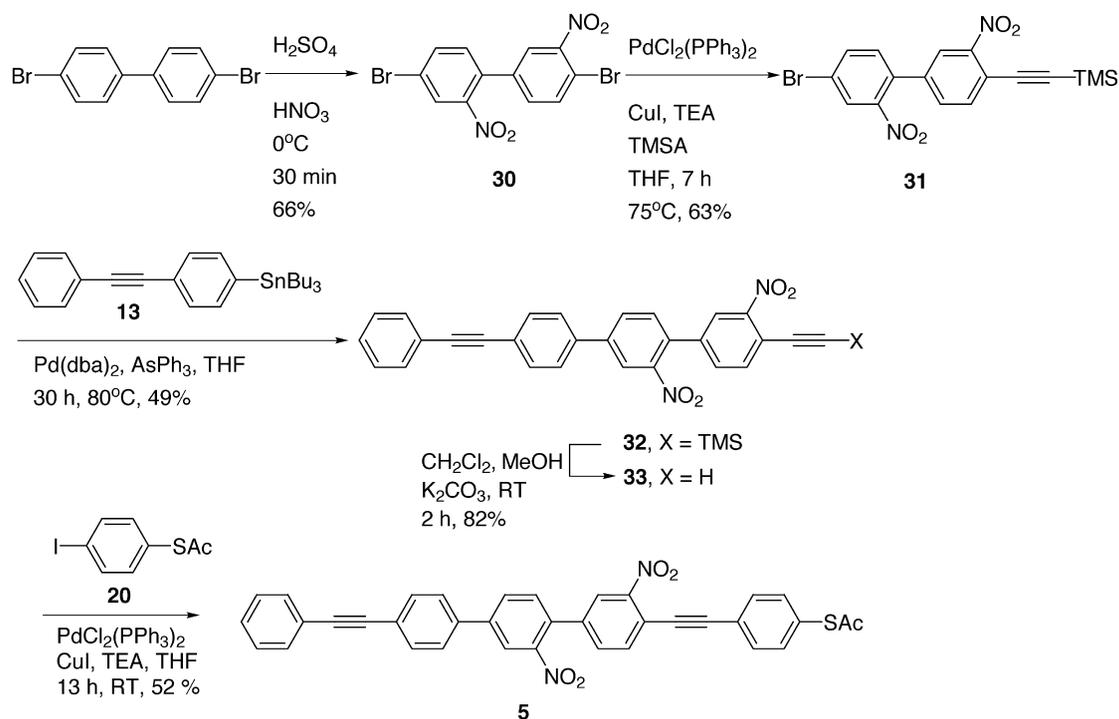
The Stille coupling conditions afforded **34** which was deprotected to form **35** in a higher than expected yield (vide supra). A final double Sonogashira coupling with the alligator clip **20** following typical conditions gave the desired double functionalized unsymmetrical dinitroterphenyl **6**.

### 3. Summary

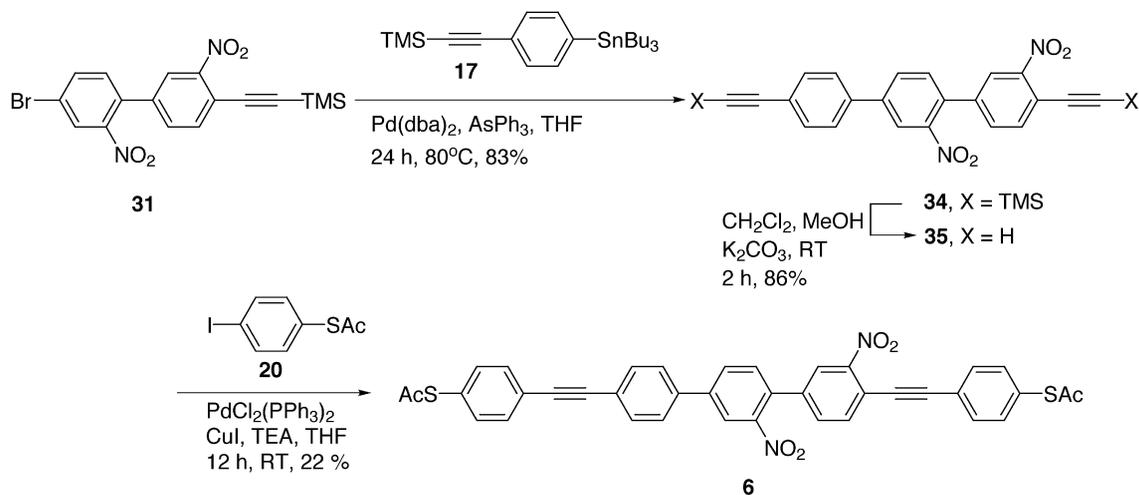
We have developed convergent synthetic methodologies that are based on Sonogashira and Stille couplings for aryl–aryl and aryl–ethynyl bond formations in order to synthesize terphenyl oligomers that are to be probed in molecular electronic device studies. In each case, the oligomers bear at least one nitro moiety for the retention of charge; a feature that has proved efficacious in molecular device activity when the compounds are configured in solid state embodiments. It is hypothesized that the terphenyl



Scheme 6.



Scheme 7.



Scheme 8.

cores, having a greater conformational twist angle at the aryl–aryl junctions, would be able to maintain charges for longer durations, thereby yielding more stable electronic devices. The hypothesis has yet to be tested; however, the syntheses described here provide the molecules, with their affixed alligator clips, making them ready for assembly and testing.

## 4. Experimental

### 4.1. Material and general procedures

Unless stated otherwise, reactions were performed in dry, nitrogen-flushed glassware, using freshly distilled solvents.

Reagent grade diethyl ether ( $\text{Et}_2\text{O}$ ) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. *N,N*-Diisopropylethylamine (Hünig's base) and triethylamine (TEA) were distilled from calcium hydride. Reagent grade *n*-hexanes, methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), methanol (MeOH), ethanol (EtOH) and ethyl acetate (EtOAc) were used without further distillation. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60  $\text{F}_{254}$  pre-coated plates (0.25 mm). In general, the chromatography guidelines reported by Still were followed.<sup>39</sup> Flash chromatography (silica gel) was performed with the indicated solvent systems using silica

gel grade 60 (230–400 mesh). All new compounds were named using the Beilstein AutoNom application of Beilstein Commander 2000 software.

#### 4.2. General procedure for the coupling of a terminal alkyne with an aryl halide utilizing a palladium–copper cross-coupling (Castro-Stephens/Sonogashira protocol)<sup>40,41</sup>

To an oven-dried screw cap tube or a round bottom flask equipped with 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). The vessel was sealed with rubber septum, evacuated and backfilled with nitrogen (3×). THF was added followed by Hünig's base or TEA. The terminal alkyne was then added and the reaction was heated if necessary. The reaction vessel was cooled to room temperature and the mixture quenched with water or a saturated solution of NH<sub>4</sub>Cl. The organic layer was diluted with organic solvent and washed with a saturated solution of NH<sub>4</sub>Cl (3×). The combined aqueous layers were extracted with organic solvent (3×), dried over anhydrous MgSO<sub>4</sub> and the solvent removed in vacuo. The crude product was then purified by flash chromatography.

#### 4.3. General procedure for the coupling of a trialkylaryl stannane with an aryl halide utilizing a palladium–arsine cross-coupling (Stille protocol)<sup>42</sup>

To an oven-dried screw cap tube or a round bottom flask equipped with a magnetic stir bar were added the aryl halide, the stannane, bis(dibenzylideneacetone)palladium(0) (5 mol% based on aryl halide) and triphenylarsine (10 mol% based on aryl halide). The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). THF was added and the reaction heated at 75 °C for at least 48 h. The reaction vessel was cooled to room temperature and the mixture quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and the solvent removed in vacuo. The crude product was then purified by flash chromatography.

#### 4.4. General procedure for alkaline deprotection of trimethylsilyl-protected alkynes

The TMS-protected alkyne was added to an open round bottom flask equipped with a stirring bar and a solution of potassium carbonate in MeOH, or tetrabutylammonium fluoride (TBAF) buffered with a mixture of acetic acid (AcOH) and acetic anhydride (Ac<sub>2</sub>O). THF or CH<sub>2</sub>Cl<sub>2</sub> were added to dissolve the organic compound. The reaction was monitored by TLC every 5 min until deprotection was complete. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and the solvent removed in vacuo. The crude product was then purified by flash chromatography.

#### 4.5. General HOF oxidation procedure<sup>32</sup>

**CAUTION!** Using the dilute form of F<sub>2</sub> in He is highly recommended to minimize potential explosions. The 20%

F<sub>2</sub> in He was purchased as a special order mixture from Air Products, Inc., and ordering of the mixture is recommended over mixing the gases in house. F<sub>2</sub>-approved fittings should be used throughout the gas manifold system. The entire apparatus should be assembled in a high flow hood.

To a polyethylene bottle was added a mixture of H<sub>2</sub>O (1 mL/mmol of substrate) and CH<sub>3</sub>CN (30 mL/mmol of substrate) and the vessel was cooled to –20 °C, before bubbling F<sub>2</sub> (20% in He) through the solution at a rate of 80 cubic centimeters per minute (ccpm) for 2 h. The resulting HOF/CH<sub>3</sub>CN solution was then purged with pre-purified He for 15 min (**CAUTION!** To avoid explosion, the He purging is essential to ensure that there is no remaining fluorine in the reaction mixture or gas lines) followed by the addition of a solution of the aniline in THF. After stirring for 20 min, the reaction was neutralized by pouring it into aq. NaHCO<sub>3</sub> and stirring for 20 min before filtering. The crude was then purified by flash chromatography.

**4.5.1. 2,5-Dibromonitrobenzene (7).**<sup>43</sup> **CAUTION!** Nitration of aromatics can lead to polynitrated compounds that are explosive. Although no explosions were seen in this study, we had a previous explosion on related compounds,<sup>43</sup> and blast-protection should therefore be used throughout this process.

Into a 3-neck 1 L round bottom flask fitted with a mechanical stirrer, dibromobenzene (118 g, 0.5 mol) was dissolved in a solution of CH<sub>2</sub>Cl<sub>2</sub> (300 mL) and sulfuric acid (200 mL). A mixture of nitric acid (90%, 46 g, 0.7 mol) and sulfuric acid (75 mL) was then added dropwise by an addition funnel, in small batches of about 5 mL every 5 min or until the strong blue color of the reaction mixture turned back into a dark yellow. The reaction mixture was monitored by GC and after 30 min the reaction was complete and quenched with a solution of 25% aq. NaOH (30 mL) to yield a light yellow organic phase. After extractions with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), the crude was washed with water (90 mL) and dried over MgSO<sub>4</sub>. Evaporation in vacuo afforded 140.4 g (98% yield) of **7** as bright light yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J*=2.2 Hz, 1H), 7.62 (q, *J*=8.6 Hz, 1H), 7.56 (d, *J*=8.6, 2.2 Hz, 1H).

**4.5.2. 2,5-Dibromoacetanilide (9).**<sup>44</sup> To a slurry of **7** (28.1 g, 100 mmol) in a 1 L round bottom flask containing a mixture of EtOH (100 mL) and THF (100 mL), was added tin(II) chloride dihydrate (113 g, 0.5 mol) in small portions, avoiding an excessive increase in the temperature. The yellow slurry was left to cool before a partial evaporation in vacuo, resulting in a white cake. The reaction mixture was transferred into a 1 L beaker containing a solution of 15% aq. NaOH (100 mL) and left for 30 min with stirring at ice bath temperature. Extractions were done with Et<sub>2</sub>O (30 mL) and the organic layers were collected and washed with brine (100 mL). Acetic anhydride (30 mL) was added to the organic solution and stirred for 10 min, and TEA (10 mL, 100 mmol) was added followed by heating at 35 °C for 1 h. The afforded white liquid was washed with 50% aq. MeOH (100 mL) and extracted with Et<sub>2</sub>O (50 mL). The volume of solvent was reduced, and crystallization with THF (300 mL) and EtOH (300 mL) furnished **8** (27 g, 92% yield) as opaque

white crystals.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (br s, 1H), 7.58 (br s, 1H), 7.38 (d,  $J=8.5$  Hz, 1H), 7.12 (dd,  $J=8.5$ , 2.3 Hz, 1H), 2.25 (s, 3H).

**4.5.3. 2,5-Dibromo-4-nitroacetanilide (10).**<sup>44</sup> Into a 500 mL 3-neck round bottom flask equipped with mechanical stirring and containing a mixture of nitric acid 90% (55 g, 80 mmol) and sulfuric acid 96% (100 mL), **9** (22 g, 75 mmol) was slowly added at  $-20^\circ\text{C}$ . The mixture was stirred until room temperature was reached. Pouring the reaction mixture into an ice bath afforded a light yellow precipitate. The solid was filtered before being washed with saturated aq. sodium bicarbonate (100 mL), water (100 mL) and MeOH (100 mL) yielding **10** (14 g, 63% yield) as a pale white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.97 (s, 1H), 8.20 (s, 1H), 7.76 (br s, 1H), 2.31 (s, 3H).

**4.5.4. 2,5-Dibromo-4-nitroaniline (11).**<sup>44</sup> Into a 500 mL round bottom flask, **10** (10 g, 30 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (160 mL). MeOH (160 mL) was added, followed by  $\text{K}_2\text{CO}_3$  (12 g, 89 mmol). Stirring the light yellow reaction mixture for 3 h resulted into a sunflower-color solution. After evaporation of the methanolic portion, water was used to wash the reaction mixture, and extractions with  $\text{CH}_2\text{Cl}_2$  (3 $\times$ 30 mL) and EtOAc (3 $\times$ 30 mL) were done before drying over  $\text{MgSO}_4$ . Crystallization from  $\text{CH}_2\text{Cl}_2$  (10 mL) and MeOH (10 mL) furnished 7.6 g (88% yield) of **11** as bright light orange crystals.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (s, 1H), 7.03 (s, 1H), 4.75 (br s, 2H).

**4.5.5. 1-Bromo-4-phenylethynyl-benzene (12).**<sup>45</sup> The Sonogashira coupling protocol was followed using 4-bromiodobenzene (2.8 g, 10 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (140 mg, 2% mol), CuI (76 mg, 4% mol), THF (15 mL), Hünig's base (7 mL, 40 mmol) and phenylacetylene (1.3 mL, 12 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  6:1) afforded **12** (2.2 g, 86% yield) as a white powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.5 (m, 2H), 7.38 (m, 5H).

**4.5.6. Tributyl-(4-phenylethynyl-phenyl)-stannane (13).** Into a 500 mL round bottom flask containing a solution of **12** (2.6 g, 10.1 mmol) in THF (200 mL), *n*-BuLi (4.0 mL, 16.1 mmol) was added dropwise at  $-78^\circ\text{C}$ , from an attached addition funnel. The reaction mixture was stirred for 45 min before adding dropwise tri-*n*-butyltin chloride (3 mL, 11.1 mmol). The reaction mixture was allowed to warm up to room temperature, quenched with water (100 mL), extracted with EtOAc (50 mL) and dried over  $\text{MgSO}_4$ . Removal of the solvent in vacuo and purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  5:1) afforded **13** (4.2 g, 87% yield) as a pale yellow liquid. IR (KBr) 2922, 2328, 2216, 1950, 1904, 1801, 1746, 1657, 1595, 1495, 1454, 1380, 1343, 1299, 1182, 1069, 1015  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (m, 2H), 7.47 (m, 4H), 7.35 (m, 2H), 1.54 (m., 6H), 1.35 (sext,  $J=7.3$  Hz, 6H), 1.0 (t,  $J=8.0$  Hz, 6H), 0.9 (t,  $J=7.3$  Hz, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.2, 136.5, 131.8, 130.9, 128.4, 123.7, 123.0, 89.9, 89.7, 29.3, 27.6, 13.9, 9.8. HRMS calcd for  $\text{C}_{26}\text{H}_{36}\text{Sn}$ : 466.1841, found: 466.1841.

**4.5.7. 4-Bromo-6-nitro-4'-phenylethynyl-biphenyl-3-ylamine (14).** The Stille coupling procedure was followed

using **11** (5.2 g, 17.5 mmol),  $\text{Pd}(\text{dba})_2$  (502 mg, 5% mol),  $\text{AsPh}_3$  (536 mg, 10% mol), THF (50 mL), and **13** (9 g, 19.3 mmol) at  $85^\circ\text{C}$  for 36 h. Purification by flash chromatography twice (hexanes/ $\text{CH}_2\text{Cl}_2$  1:1, then 8:1), yielded the desired adduct **14** (6.5 g, 95% yield) as bright yellow crystals. Mp  $172^\circ\text{C}$ . IR (KBr) 3487, 3390, 3057, 2668, 1961, 1961, 1915, 16709, 1552, 1501, 1302, 1253, 1117, 1034  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H), 7.55 (m, 4H), 7.37 (m, 3H), 7.23 (m, 2H), 6.6 (s, 1H), 4.76 (br s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 138.7, 138.5, 138.1, 131.8, 131.7, 130.6, 128.6, 128.5, 127.9, 123.2, 123.2, 116.6, 106.3, 90.5, 89.1. HRMS calcd for  $\text{C}_{20}\text{H}_{13}\text{BrN}_2\text{O}_2$ : 392.0161, found: 392.0154.

**4.5.8. 4-Bromo-2,5-dinitro-4'-phenylethynyl-biphenyl (15).** The general HOF oxidation procedure was followed using **12** (2.5 g, 6.4 mmol), THF (5 mL) and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  to yield a yellow solid as the desired product (2.4 g, 89% yield). Mp  $175^\circ\text{C}$ . IR (KBr) 3102, 3021, 2873, 2714.5, 2407, 2217, 1538, 1344, 1215, 1099  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (s, 1H), 7.92 (m, 1H), 7.60 (m, 4H), 7.37 (m, 3H), 7.33 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.3, 133.7, 132.5, 131.9, 130.7, 128.9, 128.6, 128.5, 127.9, 122.9, 114.2, 91.8, 88.4. HRMS calcd for  $\text{C}_{20}\text{H}_{11}\text{BrN}_2\text{O}_4$ : 421.9902, found: 421.9910.

**4.5.9. (4-Bromo-phenylethynyl)-trimethyl-silane (16).**<sup>46</sup> The Sonogashira coupling protocol was followed using 4-bromiodobenzene (5 g, 17.6 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (62 mg, 5% mol), CuI (33 mg, 10% mol), THF (20 mL), Hünig's base (25 mL, 43 mmol) and TMSA (3 mL, 21.3 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  6:1) afforded **16** (1.9 g, 83% yield) as a pale solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (m, 2H), 7.42 (m, 2H), 0.26 (s, 9H).

**4.5.10. Trimethyl-(4-tributylstannanyl-phenylethynyl)-silane (17).**<sup>37</sup> Into a 500 mL round bottom flask containing a solution of **16** (16.7 g, 65.8 mmol) in THF (50 mL), *n*-BuLi (30.3 mL, 72 mmol) was added dropwise at  $-78^\circ\text{C}$  from an attached addition funnel. The reaction mixture was stirred for 45 min before adding dropwise tri-*n*-butyltin chloride (21 mL, 73 mmol). The reaction mixture was allowed to warm up to room temperature, then quenched with water (100 mL), extracted with  $\text{Et}_2\text{O}$  (50 mL) and dried over  $\text{MgSO}_4$ . Purification by Kugelrohr distillation (130  $^\circ\text{C}$  at 0.25 mm Hg) and flash chromatography (hexanes) afforded **17** (27 g, 89% yield) as a clear liquid. IR (KBr) 3438, 3065, 1605, 1532, 1471, 1406, 1381, 1349, 1262, 1072, 1009  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (s, 4H), 1.53 (m, 6H), 1.34 (sext,  $J=7.5$  Hz, 6H), 1.08 (m, 6H), 0.91 (t,  $J=7.5$  Hz, 9H), 0.27 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 136.3, 131.2, 122.8, 29.5, 27.6, 13.9, 9.8, 0.2. HRMS calcd for  $\text{C}_{23}\text{H}_{40}\text{SiSn}$ : 463.1857, found: 463.1847.

**4.5.11. Trimethyl-6,9-dinitro-8-phenylethynyl-triphenyl-ethynyl-silane (18).** The Stille coupling procedure was followed using **15** (830 mg, 2 mmol),  $\text{Pd}(\text{dba})_2$  (56 mg, 5% mol),  $\text{AsPh}_3$  (16 mg, 6% mol), THF (10 mL), and **17** (1 g, 2.2 mmol) at  $85^\circ\text{C}$  for 36 h. Purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  1:2) yielded the desired adduct **18** (840 mg, 76% yield) as yellow crystals. Mp

235 °C. IR (KBr) 3439, 2959, 2151, 1529, 1476, 13.81, 1250, 851  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 1H), 7.91 (s, 1H), 7.65 (m, 2H), 7.57 (m, 4H), 7.34 (m, 1H), 7.32 (m, 1H), 0.28 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1, 136.0, 134.6, 134.3, 132.8, 128.6, 128.0, 127.9, 127.5, 127.5, 125.0, 124.8, 123.0, 0.2. HRMS calcd for  $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_4\text{Si}$ : 516.1507, found: 516.1505.

**4.5.12. 6',9'-Dinitro-8'-phenylethynyl-triphenyl-ethynyl (19).** The general deprotection protocol was followed using **18** (432 mg, 0.8 mmol), THF (10 mL), acetic acid (0.1 mL, 1.8 mmol) and TBAF (0.9 mL, 0.9 mmol) for 5 min. Purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  1:3) furnished a pale yellow solid 272 mg (73% yield). Mp 200 °C. IR (KBr) 3482, 3286, 3052, 2914, 2360, 2330, 1552, 1537, 1521, 1521, 1474, 1350, 1261  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.92 (s, 1H), 7.64 (m, 4H), 7.57 (m, 2H), 7.37 (m, 7H), 3.2 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 135.9, 135.0, 134.3, 133.0, 132.5, 131.9, 128.8, 128.6, 128.7, 127.9, 127.6, 127.6, 125.0, 123.8, 123.0, 91.7, 88.5, 82.8, 79.4. HRMS calcd for  $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_4$ : 444.1110, found: 444.1111.

**4.5.13. Thio-4-16',19'-dinitro-18'-phenylethynyl-triphenyl-ethynyl-phenyl-acetyl (1).** The Sonogashira coupling protocol was followed using **19** (240 mg, 0.5 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (21 mg, 5% mol), CuI (11 mg, 10% mol), **20** (180 mg, 0.6 mmol), THF (20 mL), and Hünig's base (0.3 mL, 2 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  1:3) afforded **1** (250 mg, 78% yield) as a yellow solid. Mp 185 °C (browning). IR (KBr) 3439.0, 2959.3, 2151.2, 1529.7, 1476.1, 1381.0, 1250.4, 851.3  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.94 (s, 1H), 7.66 (m, 4H), 7.57 (m, 4H), 7.41 (m, 9H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.5, 150.2, 150.2, 136.1, 136.0, 134.6, 134.4, 134.3, 132.5, 132.5, 132.4, 131.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.6, 127.5, 125.0, 124.6, 124.2, 123.0, 91.6, 90.8, 90.2, 88.5, 77.5, 77.2, 76.9. HRMS calcd for  $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$ : 594.1242, found: 594.1250.

**4.5.14. N-4-Iodo-phenyl-formamide (21).**<sup>47</sup> Into a 500 mL round bottom flask, 4-iodoaniline (10 g, 46 mmol) was dissolved in ethylformate (85 mL). The solution was allowed to reflux overnight, and then partially evaporated in vacuo. An additional portion of ethylformate (85 mL) was added and the process was repeated. A third portion of ethylformate (85 mL) was added and the procedure was repeated. The solvent was evaporated, and a light gray solid was isolated. Flash chromatography ( $\text{CH}_2\text{Cl}_2$ ) afforded the desired product (5 g, 45% yield) as a pale white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J=8.7$  Hz, 1H), 8.39 (d,  $J=1.6$  Hz, 1H), 7.66 (m, 4H), 7.57 (m, 4H), 7.41 (m, 9H), 2.45 (s, 3H).

**4.5.15. N-4-16',19'-Dinitro-18'-phenylethynyl-triphenyl-ethynyl-phenyl-formamide (22).** The Sonogashira coupling protocol was followed using **19** (330 mg, 0.7 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (26 mg, 5% mol), CuI (14 mg, 10% mol), **21** (220 mg, 0.9 mmol), THF (8 mL) and Hünig's base (0.4 mL, 2.9 mmol) for 12 h at 70 °C. Purification by flash chromatography ( $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  1:1.2) afforded **22** (130 mg, 31% yield) as a yellow solid with poor solubility.

Mp 270 °C (browning). IR (KBr) 3439, 3064, 2919, 2117, 1900, 1792, 1604, 1547, 1519, 1406, 1347, 1273, 1273, 1192, 1104, 1013  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ , 2.54)  $\delta$  7.95 (s, 1H), 7.94 (s, 1H), 7.66 (m, 4H), 7.57 (m, 4H), 7.41 (m, 9H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ , 40.4)  $\delta$  163.3, 160.7, 150.6, 139.7, 135.4, 135.4, 135.2, 133.6, 133.2, 132.8, 232.6, 133.2, 132.8, 132.3, 129.97, 129.6, 129.2, 129.2, 128.2, 124.3, 124.1, 122.8, 120.0, 118.0, 117.5, 117.5, 91.9, 91.7, 89.4, 88.8. HRMS calcd for  $\text{C}_{35}\text{H}_{21}\text{N}_3\text{O}_5$ : 563.1481, found: 563.1477.

**4.5.16. N-4-16',19'-Dinitro-18'-phenylethynyl-triphenyl-ethynyl-phenyl-isocynide (2).** Into a large test tube, **22** (220 mg, 0.4 mmol) and triphosgene (58 mg, 0.2 mmol) were added and sealed with septum. The tube was evacuated and nitrogen was introduced before cooling to  $-40$  °C while stirring. Distilled  $\text{CH}_2\text{Cl}_2$  (7 mL) was added until the suspension was homogeneous. Tetrabutylammonium chloride (11 mg, 0.04 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (4 mL) and added to the reaction mixture, leaving it for 30 min while monitoring by TLC. The same amount of triphosgene was added in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) before warming to 0 °C over 1.5 h. The reaction mixture then was quenched with water (10 mL), extracted with  $\text{CH}_2\text{Cl}_2$  and dried over  $\text{MgSO}_4$  before removal of the solvent in vacuo. The remaining solid was then recrystallized ( $\text{CH}_2\text{Cl}_2/\text{hexanes}$  1:1) yielding a yellow solid (90 mg, 40% yield) as the desired product. Mp 235 °C. IR (KBr) 3439, 2959, 2151, 1529, 1476, 1381, 1250, 851  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.94 (s, 1H), 7.66 (m, 4H), 7.57 (m, 4H), 7.41 (m, 9H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.5, 150.2, 150.2, 136.1, 136.0, 134.6, 134.4, 134.3, 132.5, 132.5, 132.4, 131.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.6, 127.5, 125.0, 124.6, 124.2, 123.0, 91.6, 90.8, 90.2, 88.5, 77.5, 77.2, 76.9. HRMS calcd for  $\text{C}_{35}\text{H}_{19}\text{N}_3\text{O}_4$ : 545.1376, found: 545.1378.

**4.5.17. 1,4-Dibromo-2,5-dinitro-benzene (23).**<sup>32</sup> The general HOF oxidation procedure was followed using **11** (1.9 g, 6.4 mmol), THF (15 mL) and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  to yield a yellow solid as the desired product (2 g, 70% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (s, 2H).

**4.5.18. 1,4-Dinitro-2,5-bis-trimethylsilylethynyl-phenyl-benzene (24).** The general Stille coupling procedure was followed using **22** (530 mg, 1.62 mmol),  $\text{Pd}(\text{dba})_2$  (93 mg, 10% mol),  $\text{AsPh}_3$  (100 mg, 20% mol), THF (10 mL), **17** (1.65 g, 3.6 mmol) at 75 °C for 21 h. Flash chromatography (hexanes/ $\text{CH}_2\text{Cl}_2$  5:6) yielded the desired adduct (620 mg, 75% yield) as pale yellow crystals. Mp 250 °C (browning). IR (KBr) 3430, 3267, 2960, 2883, 2155, 1530, 1477, 1411, 1357, 1251, 1223, 1185, 1116, 1014  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 1H), 7.91 (s, 1H), 7.65 (m, 2H), 7.57 (m, 4H), 7.34 (m, 1H), 7.32 (m, 1H), 0.28 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 150.2, 136.1, 134.6, 132.8, 127.9, 127.5, 124.8, 104.0, 96.9, 0.0. HRMS calcd for  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_4\text{Si}_2$ : 512.1588, found: 512.1580.

**4.5.19. 1,4-Dinitro-2,5-bis-ethynyl-phenyl-benzene (25).** The deprotection protocol was followed using **24** (615 mg, 1.2 mmol), THF (20 mL), acetic acid (0.15 mL, 2.6 mmol), and TBAF (2.8 mL, 2.8 mmol). After 10 min a light yellow solid precipitated. After addition of hexanes (10 mL) and filtration, a pale yellow solid was collected (115 mg, 27%

yield) as the desired product **25**. The compound was poorly soluble and it was taken, without complete characterization, onto the next step with no further purification. Mp 270 °C. IR (KBr) 3277, 3052, 2960, 2871, 2359, 1932, 1813, 1675, 1531, 1477, 1355, 1278, 1262, 1012 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (s, 2H), 7.62 (m, 4H), 7.35 (m, 4H), 3.20 (s, 2H). HRMS calcd for C<sub>22</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, 368.0800, found: 368.0797.

**4.5.20. Thioacetic acid S-{4-[4''-(4-acetylsulfanyl-phenylethynyl)-2',5'-dinitro-[1,1';4',1'']terphenyl-4-ylethynyl]-phenyl} ester (3).** The Sonogashira coupling protocol was followed using **24** (110 mg, 0.3 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (21 mg, 10% mol), CuI (11 mg, 20% mol), **20** (200 mg, 0.41 mmol), THF (7 mL) and Hünig's base (0.3 mL, 2.4 mmol) for 12 h at 70 °C. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:3) afforded **3** (120 mg, 60% yield) as a yellow solid with poor solubility. Mp 190 °C (browning). IR (KBr) 3399.5, 3062.8, 2956.6, 2924.0, 2853.5, 2357.6, 1909.9, 1707.5, 1603.6, 1587.9, 1536.1, 1484.5, 1351.6, 1117.6 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 2H), 7.62 (m, 8H), 7.41 (m, 8H), 2.45 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.5, 150.2, 136.1, 134.4, 32.5, 132.4, 128.7, 128.1, 127.6, 124.5, 124.2, 90.8, 90.1, 27.1. HRMS calcd for C<sub>36</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>S: 594.1242, found: 594.1249.

**4.5.21. 4-Iodo-2-nitro-phenylamine (26).**<sup>36</sup> Into a 500 mL round bottom flask were dissolved 2-nitroaniline (30 g, 217 mmol), NaOAc (18.7 g, 228 mmol) and acetic acid (150 mL). A solution of ICl (37 g, 228 mmol) in acetic acid (100 mL) was added and the reaction mixture heated at 90 °C for 30 min. After cooling, the slurry was poured into ice water to afford a brown precipitate that was filtered giving the desired product (53 g, 93% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J*=2 Hz, 1H), 7.56 (dd, *J*=2, 8.2 Hz, 1H), 6.61 (*J*=8.2 Hz, 1H), 6.1 (br s, 2H).

**4.5.22. Nitrosonium tetrafluoroborate (NOBF<sub>4</sub>).**<sup>9</sup> Into a 3-neck 2 L round bottom flask fitted with a mechanical stirrer was added nitrogen purged acetic anhydride (614 mL) and the flask was cooled to -20 °C. HBF<sub>4</sub> (50%, 213 g, 1.2 mol) was added in small portions, so as to maintain the temperature. The emulsion was stirred for 15 min and then warmed to 0 °C. Sodium nitrite (138 g, 2 mol) in H<sub>2</sub>O (ca. 100 mL) was slowly and carefully added from an addition funnel to a 1 L 3-neck round bottom flask containing nitric acid 69% (200 g, 2.2 mol) while maintaining rapid stirring. The resulting brown fumes were trapped in a tubing-connected cold finger at -78 °C to afford a blue ink-colored solution. This concentrated NO<sub>x</sub> species was then slowly added to the tetrafluoroboric acid solution until the blue color persisted. The precipitate was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> while kept under a nitrogen atmosphere. The resulted white crystals were left under vacuum overnight and stored under a nitrogen atmosphere, affording the desired product (67 g, 48% yield) as a fluffy white solid, which was used as is for further reactions.

**4.5.23. 2,4-Diodo-nitrobenzene (27).**<sup>48</sup> Into a 500 mL round bottom flask, NOBF<sub>4</sub> (4.87 g, 416 mmol) was added. CH<sub>3</sub>CN (180 mL) was added and the mixture was cooled to -40 °C. In a 250 mL round bottom flask was dissolved **25** (10 g, 378 mmol) in CH<sub>3</sub>CN (80 mL) and the mixture was

slowly transferred via cannula to the first vessel. After 30 min, the reaction mixture was allowed to warm briefly to 0 °C, followed by cooling to -40 °C, and small portions of a mixture of NaI (11.3 g, 76 mmol) and iodine (9.6 g, 38 mmol) were added over 30 min before diluting with CH<sub>2</sub>Cl<sub>2</sub>, washed with water (2×300 mL), aq. NaHSO<sub>3</sub> (2×250 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Partial evaporation of the solvent and slow addition of hexanes caused the precipitation of a light pale yellow solid (10.3 g, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J*=8 Hz, 1H), 7.73 (d, *J*=8 Hz, 1H), 7.43 (m, 2H), 7.38 (m, 3H), 7.31 (dd, *J*=8, 2 Hz, 1H).

**4.5.24. 1,4-Di(4'-trimethylsilylethynyl-phenyl)-2-nitrobenzene (28).** The Stille coupling procedure was followed using **27** (2 g, 6.1 mmol), Pd(dba)<sub>2</sub> (107 mg, 3% mol), AsPh<sub>3</sub> (114 mg, 6% mol), THF (30 mL), and **17** (6 g, 13 mmol) at 85 °C for 36 h. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) yielded the desired adduct **28** (2.1 g, 68% yield) as a fluffy light yellow solid. Mp 165 °C. IR (KBr) 3017, 2963, 2881, 2400, 2147, 1514.5, 1479, 1425, 1351, 1246, 1215, 1102, 1009 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J*=2 Hz, 1H), 7.84 (dd, *J*=2, 8 Hz, 1H), 7.54 (m, 2H), 7.49 (d, *J*=8 Hz, 1H), 7.28 (m, 2H), 0.28 (s, 9H), 0.27 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.7, 141.2, 138.2, 137.3, 134.8, 133.0, 132.6, 132.6, 130.8, 128.1, 127.0, 123.8, 123.6, 122.8, 104.7, 104.6, 96.4, 95.9, 0.2. HRMS calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>2</sub>Si<sub>2</sub>: 467.1737, found: 467.1735.

**4.5.25. 1,4-Di(4'-ethynyl-phenyl)-2-nitrobenzene (29).** The deprotection protocol was followed using **28** (1.9 g, 4 mmol), CH<sub>2</sub>Cl<sub>2</sub> (20 mL), MeOH (25 mL) and K<sub>2</sub>CO<sub>3</sub> (2.8 g, 20.3 mmol) for 30 min. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) furnished a yellow solid (1.1 g, 86% yield) as the desired product. Mp 180 °C. IR (KBr) 3297, 3021, 2924.2, 2854, 2431, 2396, 2104, 1526, 1471, 1417, 1355, 1215 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J*=1.6 Hz, 1H), 7.83 (dd, *J*=1.6, 8 Hz, 1H), 7.62 (m, 4H), 7.56 (m, 2H), 7.51 (d, *J*=8 Hz, 1H), 7.32 (m, 2H), 3.19 (s, 1H), 3.16 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.6, 141.1, 138.5, 137.6, 134.7, 133.1, 132.6, 132.5, 130.8, 128.1, 127.1, 122.8, 122.7, 122.5, 83.2, 78.9, 78.6. HRMS calcd for C<sub>22</sub>H<sub>13</sub>NO<sub>2</sub>: 323.0946, found: 323.1155.

**4.5.26. 2,5-Bis-thioacetylphenyl-ethynylphenyl-nitrobenzene (4).** The Sonogashira protocol was followed using **29** (500 mg, 1.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (55 mg, 10% mol), CuI (30 mg, 20% mol), **20** (903 mg, 3.2 mmol), THF (10 mL) and TEA (1.7 mL, 12.4 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) afforded **4** (550 mg, 58% yield) as a light yellow solid. Mp 190 °C (browning). IR (KBr) 3677, 3615, 3017, 2427, 2392, 2205, 1704, 1514, 1421, 1343, 1219, 1110, 1071 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J*=1.6 Hz, 1H), 7.88 (dd, *J*=1.6, 8 Hz, 1H), 7.68 (s, 4H), 7.59 (m, 6H), 7.54 (d, *J*=8 Hz, 1H), 7.38 (m, 4H), 7.36 (m, 2H), 2.46 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 193.8, 141.3, 138.4, 137.5, 135.0, 149.9, 134.6, 134.6, 132.9, 132.8, 132.6, 132.6, 132.4, 130.9, 128.7, 128.6, 128.4, 127.4, 124.7, 124.6, 123.8, 123.5, 123.0, 90.8, 90.6, 90.2, 30.7, 30.7. HRMS calcd for C<sub>36</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>S: 623.7414, found: 623.1225.

**4.5.27. 2,3'-Dinitro-4,4'-dibromobiphenyl (30).**<sup>37</sup> Into a 500 mL round bottom flask, 4,4'-dibromo-biphenyl (24 g, 0.3 mol) was dissolved in H<sub>2</sub>SO<sub>4</sub> (150 mL) and the flask was cooled to 0 °C, followed by a slow addition of fuming HNO<sub>3</sub> (183 mL). The clear yellow solution turned into a bright yellow suspension, and it was stirred for an additional 30 min. After pouring it into ice water and filtering, the solid was dissolved into EtOH (ca. 300 mL), heated and the volume of the solvent reduced. Crystallization upon cooling and filtration afforded the desired product **30** (18.3 g, 66% yield) as a light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J*=2 Hz, 1H), 7.81 (m, 6H), 7.32 (m, 4H).

**4.5.28. (4'-Bromo-3,2'-dinitro-biphenyl-4-ylethynyl)-trimethyl-silane (31).** The Sonogashira protocol was followed using **30** (5 g, 12.4 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (175 mg, 2%), CuI (95 mg, 4%), TEA (8.6 mL, 50 mmol), TMSA (1.85 mL, 13 mmol) and THF (50 mL) at 75 °C for 24 h. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 2:1) gave a light yellow solid that was recrystallized (hexanes/CH<sub>2</sub>Cl<sub>2</sub>) to yield **31** (3.1 g, 63% yield). Mp 102 °C. IR (KBr) 3013, 2955, 2916, 2846, 2403, 2159, 1600, 1526, 1460, 1355, 1262, 1211, 1157, 1079 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J*=4 Hz, 1H), 7.98 (d, *J*=4 Hz, 1H), 7.83 (dd, *J*=4, 8 Hz, 1H), 7.70 (d, *J*=8 Hz, 1H), 7.44 (dd, *J*=4, 8 Hz, 1H), 7.32 (d, *J*=8 Hz, 1H), 0.29 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.7, 136.3, 135.5, 133.1, 132.7, 132.1, 128.0, 124.2, 123.2, 118.7, 105.8, 104.2, 99.0, -0.2. HRMS calcd for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>Si: 417.9985, found: 414.9990.

**4.5.29. (3,2'-Dinitro-4''-phenylethynyl-[1,1';4',1''] terphenyl-4-ylethynyl)-trimethyl-silane (32).** The Stille coupling procedure was followed using **31** (1.5 g, 3.6 mmol), Pd(dba)<sub>2</sub> (178 mg, 5% mol), AsPh<sub>3</sub> (110 mg, 10% mol), THF (30 mL) and **13** (1.8 g, 3.7 mmol) at 75 °C for 30 h. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) yielded the desired adduct **32** (0.9 g, 49% yield) as a yellow solid. Mp 235 °C. IR (KBr) 3021, 2963, 2920, 2846, 2400, 2213, 2163, 1600, 1526, 1471, 1413, 1347, 1203, 1079, 1017 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J*=1.6 Hz, 1H), 8.05 (d, *J*=1.6 Hz, 1H), 7.92 (dd, *J*=1.6, 8 Hz, 1H), 7.70 (m, 5H), 7.56 (m, 4H), 7.38 (m, 3H), 0.31 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.3, 149.0, 142.4, 138.5, 137.4, 135.5, 132.6, 132.5, 132.3, 131.8, 131.8, 131.2, 128.8, 128.6, 128.6, 127.1, 124.3, 123.1, 118.4, 105.5, 99.2, 91.4, -0.1. HRMS calcd for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>Si: 516.1505, found: 516.1511.

**4.5.30. 4-Ethynyl-3,2'-dinitro-4''-phenylethynyl-[1,1';4',1'']terphenyl (33).** The deprotection protocol was followed using **32** (500 mg, 0.9 mmol), CH<sub>2</sub>Cl<sub>2</sub> (40 mL), MeOH (40 mL) and K<sub>2</sub>CO<sub>3</sub> (640 mg, 4.6 mmol) for 30 min. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:1.5) furnished a yellow solid **33** (350 mg, 82% yield). Mp 200 °C. IR (KBr) 3300, 3013, 2434, 2396, 1607, 1526, 1464, 1417, 1343, 1215, 1029 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J*=2 Hz, 1H), 8.09 (d, *J*=2 Hz, 1H), 7.93 (dd, *J*=2, 8.4 Hz, 1H), 7.76 (d, *J*=2 Hz, 1H), 7.67 (m, 4H), 7.56 (m, 4H), 7.38 (m, 3H), 3.61 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.0, 142.5, 139.2, 137.4, 135.9, 132.7, 132.57, 132.5, 132.4, 131.9, 131.3, 128.8, 128.6, 127.2, 124.5, 125.4, 123.3, 123.1, 117.5, 91.5, 88.8, 86.5,

78.4. HRMS calcd for C<sub>28</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: 444.1110, found: 444.1114.

**4.5.31. Thioacetic acid S-[4-(3,2'-dinitro-4''-phenylethynyl-[1,1';4',1''] terphenyl-4-ylethynyl)-phenyl] ester (5).** The Sonogashira protocol was followed using **33** (160 mg, 0.4 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (25 mg, 10% mol), CuI (14 mg, 20% mol), **20** (105 mg, 0.4 mmol), THF (10 mL), and TEA (0.3 mL, 1.4 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:1.5) afforded **5** (54 mg, 52% yield) as a yellow solid with poor solubility. 150 °C (browning). IR (KBr) 3013, 2438, 2403, 2217, 1712, 1600, 1522, 1417, 1339, 1219, 1110, 1079 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J*=1.6 Hz, 1H), 8.14 (d, *J*=1.6 Hz, 1H), 7.93 (dd, *J*=1.6, 8.4 Hz, 1H), 7.67 (m, 5H), 7.57 (m, 4H), 7.45 (m, 2H), 7.39 (m, 3H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.3, 136.2, 142.48, 138.5, 135.0, 134.4, 132.8, 132.6, 132.6, 132.5, 131.8, 131.3, 128.8, 128.6, 127.2, 124.6, 124.40, 123.6, 123.3, 123.1, 118.5, 118.3, 91.5, 87.8, 86.4, 83.7, 30.5. HRMS calcd for C<sub>36</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>S: 594.1249, found: 594.1240.

**4.5.32. 3,2'-Dinitro-4''-4-di(trimethylsilanylethynyl)-[1,1';4',1'']terphenyl (34).** The Stille coupling procedure was followed using **31** (2 g, 4.7 mmol), Pd(dba)<sub>2</sub> (83 mg, 3% mol), AsPh<sub>3</sub> (88 mg, 6% mol), THF (30 mL), and **17** (2.6 g, 5.7 mmol) at 75 °C for 34 h. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:1) yielded the desired adduct **34** (2 g, 83% yield) as a fluffy yellow solid. Mp 138 °C. IR (KBr) 3013, 2955, 2920, 2846, 2400, 2155, 1638, 1533, 1464, 1429, 1355, 1219, 1087, 1017 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J*=1.6 Hz, 1H), 8.04 (d, *J*=2 Hz, 1.6 Hz, 1H), 7.90 (dd, *J*=1.6, 8 Hz, 1H), 7.71 (d, *J*=8 Hz, 1H), 7.51 (m, 2H), 0.30 (s, 9H), 0.29 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.4, 149.1, 142.4, 138.6, 137.7, 135.6, 133.1, 132.7, 132.6, 132.4, 131.4, 127.1, 124.4, 124.2, 123.3, 118.5, 105.6, 104.5, 99.3, 96.7, 0.2, -0.1. HRMS calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: 512.1588, found: 512.1594.

**4.5.33. 4''-Ethynyl-3,2'-dinitro-[1,1';4',1'']terphenyl-4-ylethyne (35).** The deprotection protocol was followed using **34** (1.9 g, 4 mmol), CH<sub>2</sub>Cl<sub>2</sub> (20 mL), MeOH (25 mL) and K<sub>2</sub>CO<sub>3</sub> (2.8 g, 20.3 mmol) for 30 min. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) furnished a yellow solid (1.1 g, 86% yield) as the desired product. Mp 320 °C (browning). IR (KBr) 3281, 3009, 2924, 2846, 2438, 2400, 2104, 1615, 1522, 1417, 1335, 1211, 1071, 1021 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J*=2 Hz, 1H), 8.10 (d, *J*=2 Hz, 1H), 7.92 (dd, *J*=2, 8 Hz, 1H), 7.77 (d, *J*=8 Hz, 1H), 7.65 (m, 4H), 7.54 (m, 2H), 3.62 (s, 1H), 3.22 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.0, 142.4, 139.1, 138.1, 135.9, 133.2, 133.2, 132.6, 1323.5, 131.4, 127.2, 124.5, 123.4, 123.1, 117.5, 86.5, 83.0, 79.2, 78.4. HRMS calcd for C<sub>22</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: 368.0797, found: 368.0801.

**4.5.34. Thioacetic acid S-{4-[4-(4-acetylsulfanyl-phenylethynyl)-3,2'-dinitro-[1,1';4',1''] terphenyl-4''-ylethynyl]-phenyl} ester (6).** The Sonogashira coupling protocol was followed using **35** (500 mg, 1.3 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (50 mg, 50% mol), CuI (26 mg, 20% mol), **20** (105 mg,

0.3 mmol), THF (10 mL), and TEA (1.5 mL, 11 mmol) for 12 h at room temperature. Purification by flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 1:2) afforded **6** (150 mg, 22% yield) as a dark yellow solid. Mp 140 °C (browning). IR (KBr) 3013, 2403, 2201, 1704, 1592, 1522, 1429, 1347, 1211, 1122, 1075 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J*=2 Hz, 1H), 8.15 (d, *J*=2 Hz, 1H), 7.94 (dd, *J*=2, 7.6 Hz, 1H), 7.8 (d, *J*=7.6 Hz, 1H), 7.66 (m, 6H), 7.58 (m, 4H), 7.45 (dd, *J*=2, 7.6 Hz, 4H), 2.465 (s, 3H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 193.5, 151.3, 150.1, 142.6, 138.7, 137.9, 135.2, 134.7, 134.7, 133.0, 132.9, 132.8, 132.6, 131.5, 129.9, 129.8, 128.8, 127.4, 124.9, 124.5, 124.2, 123.8, 118.7, 96.4, 90.9, 90.7, 86.4, 30.7, 30.7. HRMS calcd for C<sub>38</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: 668.1076, found: 668.1096.

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