Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 62 (2006) 10303–10310
Tetrahedron

Syntheses of new functionalized azobenzenes for potential molecular electronic devices

Byung-Chan Yu,[a,†] Yasuhiro Shirai[b] and James M. Tour[b,*]

[a]Department of Chemistry, Mokwon University, Daejon 302-729, Republic of Korea
[b]Department of Chemistry and The Smalley Institute for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main Street, Houston, TX 77005, USA

Received 18 May 2006; revised 14 August 2006; accepted 21 August 2006

Abstract—New non-symmetrical azobenzene derivatives have been synthesized as potential molecular electronic switching device candidates. The Oxone® mediated oxidation of anilines provided nitroso-functionalized arenes, which were then condensed with substituted anilines to provide a series of azobenzene derivatives that could be further converted into oligo(phenylene ethynylene)s or diazonium salts. The resulting thiolacetates, thiols, or diazonium salts are capable of forming molecular layers on the surface of gold or silicon, thereby paving the way for molecular electronics testing.

1. Introduction

Molecular electronics is a promising area of research that focuses on a bottom-up strategy to fabricate nanoscopic electronic devices based on self-assembled monolayers (SAMs) of organic molecules on surfaces.[1] One of the classes of compounds we have concentrated on is a series of oligo(phenylene ethynylene) (OPE) derivatives that have enabled the study of molecular switching processes in electronic devices.[1,2]

Alternatively, the self-assembly of photo-responsive molecules onto the substrates creates the possibility of using switching devices as photo-responsive components in optical storage and molecular recognition applications.[3] Azobenzene derivatives are interesting molecular device candidates that have been widely investigated due to their non-degradative reversible trans–cis photoisomerization during repeated switching cycles; azobenzenes also possess useful electrochemical activity.[4] Accordingly, the isomerization of azobenzene derivatives has been observed under the influence of an external electric field at the single molecule level.[5]

Previously we have shown that symmetrical azobenzene OPEs bearing protected thiol end groups form SAMs on metal surfaces.[2e] We envisioned that the synthesis of non-symmetrical azobenzene derivatives could be realized by changing the substituents (R_1 and R_2 in **A**, Fig. 1) of

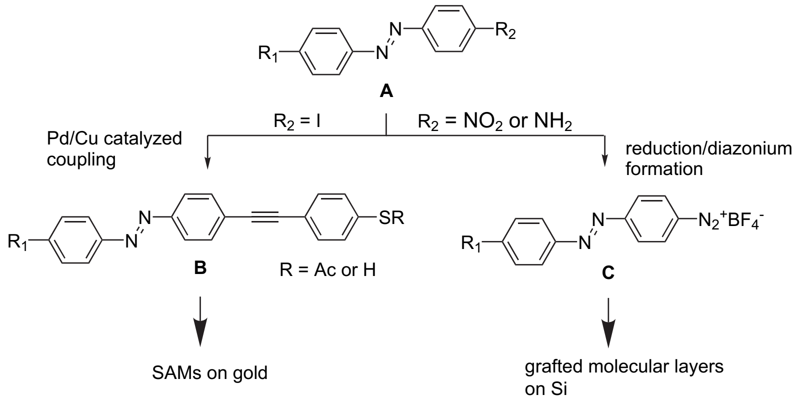


Figure 1. Synthesis of azobenzene derivatives **B** (for self-assembly on gold) or **C** (for grafting of molecular layers on silicon) from disubstituted azobenzene **A**.

---

[*] Corresponding author. Tel.: +1 713 348 6246; fax: +1 713 348 6250; e-mail: tour@rice.edu
[†] While on sabbatical leave to Rice University.

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.08.069

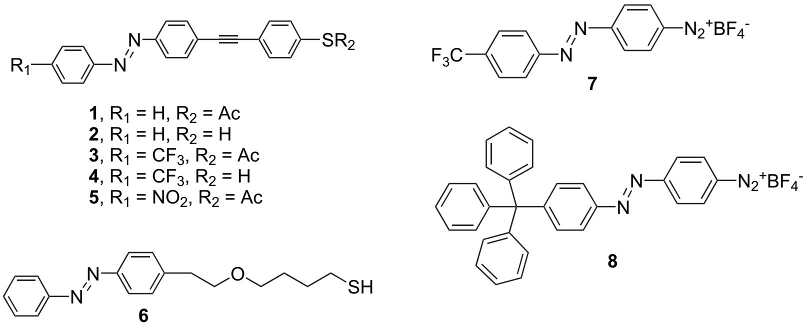


Figure 2. The structures of the type **B** azobenzene OPEs **1**–**5**, azobenzene alkanethiol **6** and type **C** azobenzene diazonium salts **7** and **8** synthesized in this work.

a disubstituted azobenzene. The resulting products would lead to an azobenzene OPE thiol/thioacetate that could form SAMs on many metal surfaces through compound **B**[1,2] or alternatively to an azobenzene diazonium salt **C** for grafting of molecular layers on semiconductor surfaces (Fig. 2).[6]

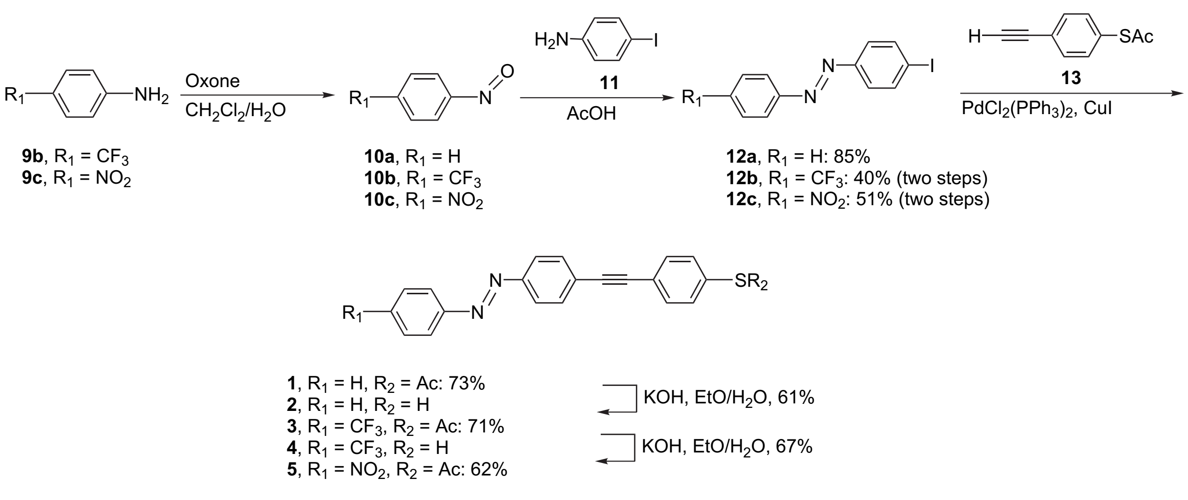
2. Results

2.1. Syntheses of azobenzene derivatives of type B

Functionalized azobenzene OPEs bearing free thiol or protected thiol end groups are preferred for formation of SAMs on gold substrates. Therefore the azobenzene OPEs **1**–**5** were prepared. After some preliminary experiments, the Oxone® mediated oxidation of anilines **9b**,**c** to provide nitrosoarenes **10a**–**c**,[7] followed by condensation with iodoaniline **11**, was found to be an efficient path to prepare a series of azobenzene derivatives. For example, the nitrosobenzene **10a** (Scheme 1, prepared from aniline[7]) was treated with **11** in acetic acid to afford the iodoazobenzene **12a**. This was coupled with thioacetate **13**[1,8] to give the protected azobenzene OPE **1**. The thioacetate **1** was carefully treated with aqueous potassium hydroxide in ethanol under an oxygen-free atmosphere (to minimize the oxidative coupling of the thiol) to provide the azobenzene OPE thiol **2** in 61% yield.

It is known that the relative order of the formed SAMs and the photo responsiveness of the molecules are dependent on the substituent at the *para* position of the azobenzene moieties comprising the SAM.[9] Therefore *para*-substituted azobenzene OPEs **3**–**5** were prepared. It was expected that the SAMs formed from **3** or **4** would show changes in wettability depending on whether the molecules were in their trans (hydrophobic) or cis (hydrophilic) forms. Since the trans and cis isomers also have different dipole moments,[10] it is possible that isomerization of the molecules in the SAMs could change the electrical properties of the SAM. With that in mind, we prepared **3** and **4** (Scheme 1). Commercially available 4-trifluoroaniline **9b** was smoothly oxidized using Oxone® to afford the nitrosobenzene **10b**, which was subsequently condensed with **11** in acetic acid to give the iodoazobenzene **12b**. Coupling to **13** gave **3**, which was converted to the corresponding thiol **4** as previously described.

In a similar fashion, the nitro-substituted azobenzene OPE **5**, which might show enhanced switching characteristics due to the electron-withdrawing nature of the nitro group, was prepared by oxidation of **9c** to **10c** using Oxone®, followed by condensation with **11** to give **12c**. The Oxone® mediated oxidation is noteworthy because nitrosobenzenes containing electron-withdrawing groups at the *para* position are difficult to prepare on a large scale.[7] Compound **12c** was subsequently coupled with the thioacetate **13** to afford the nitroazobenzene OPE **5**. Compounds **3**–**5** are currently being tested by our collaborators using scanning tunneling microscopy (STM) to detect switching effects at the single molecular level.[2f–g]



Scheme 1. Synthesis of the azobenzene OPEs **1**–**5**.

Azobenzenes bearing an alkanethiol functional group have been used to study molecular photo-switching at the nanoscale in SAMs.[4] To test single molecular switching by STM we prepared the azobenzene alkanethiol **6**. Compound **10a** was condensed with hydroxyethyl aniline (**14**) in acetic acid. The resulting alcohol was alkylated using dibromobutane in the presence of excess NaH in DMF. The alkylation, which was sluggish at room temperature, afforded the bromide **16**. Subsequent conversion of the bromide into the thiol **6** was accomplished by addition of thiourea followed by treatment with aqueous potassium hydroxide (Scheme 2).

2.2. Syntheses of azobenzene derivatives of type C

The formation of grafted molecular layers on silicon is important due to the possibility of integrating molecular electronics into existing silicon microelectronic architectures.[11] The Si–C bond is both thermodynamically and kinetically stable due to the high bond strength and low polarity of the bond.[11a] Covalent attachment of arenes via aryldiazonium salts to hydride-passivated Si⟨111⟩ and Si⟨100⟩ has been successfully demonstrated.[6] Until now few methods concerning the preparation of azobenzene molecular layers on silicon surfaces have been reported.[11b] Therefore we synthesized new functionalized azobenzene diazonium salts for grafting azobenzene derivatives onto Si substrates.

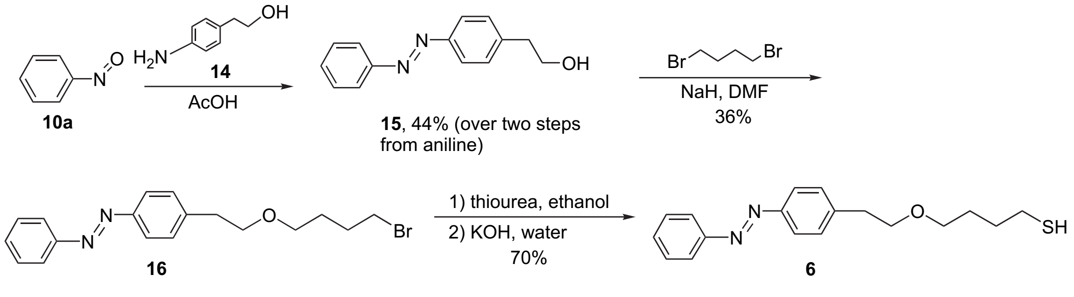
4-Trifluoromethylnitrosobenzene (**10b**) was condensed with *p*-phenylenediamine to afford **18**. The resultant amine was converted into the desired diazonium salt **7** upon treatment with boron triflouride-diethyl etherate and *tert*-butylnitrite (Scheme 3).

The tritylazobenzene diazonium salt **8** was prepared in a similar manner (Scheme 4). Commercially available 4-nitroaniline **19** was oxidized with Oxone® to afford 4-nitronitrosobenzene **20**. Without purification the labile nitroso compound was directly submitted to an acetic acid mediated condensation reaction with 4-tritylaniline (**21**) to provide 4-tritylnitroazobenzene (**22**) in 82% yield over two steps. Reduction of the nitro group to the corresponding amine **23** in the presence of the diazo moiety was accomplished by treatment with sodium sulfide in a mixture of refluxing dioxane, ethanol and water.[12] The amine **23** was subsequently converted into the air stable diazonium salt **8** upon the treatment with boron triflouride-diethyl etherate and *tert*-butylnitrite.

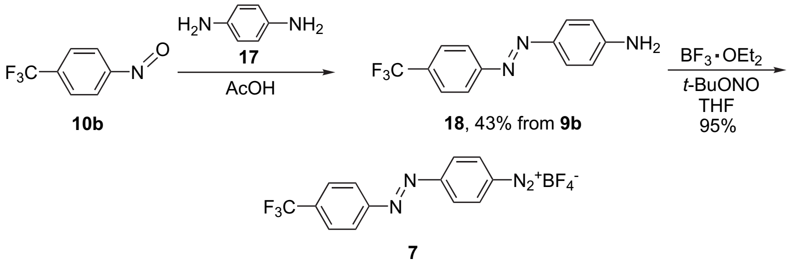
Additional examples of the synthesis of disubstituted azobenzenes are shown in Table 1. Oxidation of 4-substituted anilines by Oxone® followed by condensation of the resulting nitrosobenzenes with 4-substituted anilines provides 4,4′-disubstituted azobenzenes in 40–93% yields. The excellent yield of 4′-bromo-4-iodoazobenzene (entry 8) is particularly noteworthy because the compound could be useful for non-symmetric azobenzene OPE synthesis.[13] The azobenzenes formed were generally insoluble in acetic acid; a different work-up procedure was used for those products that were soluble (see Section 4). Formation of the corresponding nitrosobenzene from 4-trimethylsilylethynylaniline followed by coupling with **11** to provide the corresponding 4′-trimethylsilyliodoazobenzene could be useful for more advanced azobenzene OPE oligomers (entry 9).

3. Summary

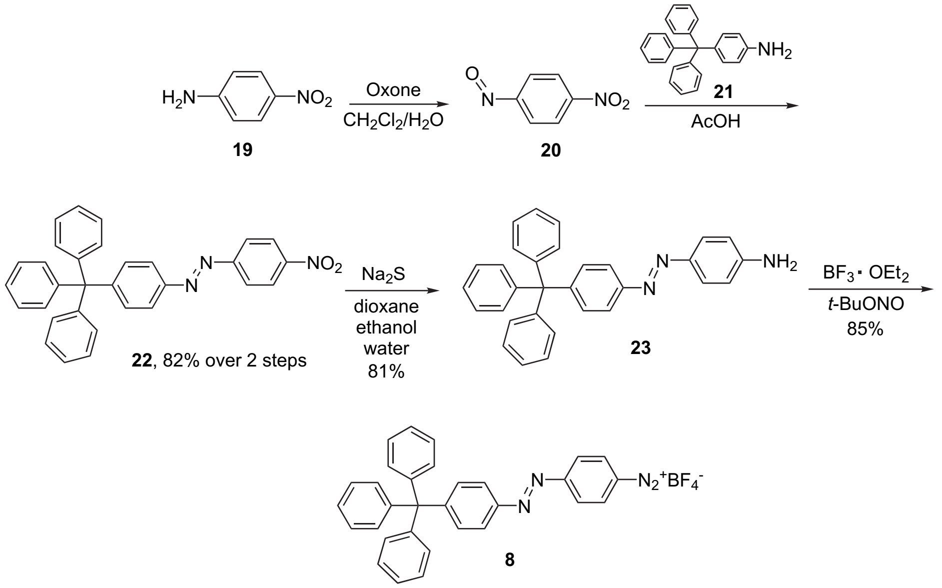
In summary, the methodology detailed here provides versatile synthetic pathways to azobenzene derivatives that could be used as potential molecular electronic or photo-responsive nanoscale devices. Work is currently underway to evaluate these photo-responsive azobenzene derivatives for their effectiveness as molecular switches integrated in nanoscale devices.



Scheme 2. Synthesis of the azobenzene alkanethiol **6**.

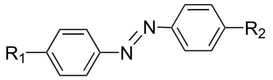


Scheme 3. Synthesis of the trifluoromethyldiazobenzene diazonium salt **7**.



Scheme 4. Synthesis of the trityldiazobenzene diazonium salt **8**.

Table 1. Synthesis of the *para*-disubstituted azobenzenes



Entry	Product	R_1	R_2	Yield (%)[a]
1	**12a**	H	I	85
2	**12b**	CF_3	I	40
3	**12c**	NO_2	I	51
4	**15**	H	$(CH_2)_2OH$	44
5	**18**	CF_3	NH_2	43
6	**22**	NO_2	Trityl	82
7	**24**	Br	H	74
8	**25**	Br	I	93
9	**26**	TMS–≡	I	35
10	**27**	NO_2	$(CH_2)_2OH$	72

[a] All yields are based on the two-step reaction sequence from the aniline except entry 1.

4. Experimental

4.1. General synthetic methods

Unless stated otherwise, reactions were performed in oven-dried, nitrogen flushed glassware equipped with a magnetic stir bar using freshly distilled solvents. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triethylamine (TEA) was distilled from calcium hydride. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. and Petra Chemical. Compound **13** was prepared as described previously.[1] All other commercially available reagents were used as received. Unless otherwise noted, reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 precoated plates (0.25 mm). Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230–400 mesh). NMR chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS) or relative to the known value of residual solvent signal. Mass spectroscopy was performed at the Rice University or University of South Carolina Mass Spectroscopy Laboratory. Melting point values are uncorrected. Compounds were named using the Struct=Name algorithm in ChemDraw 9.0 developed by CambridgeSoft.

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)[8]

To a screw cap tube or a round-bottom flask were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol % based on aryl halide), and copper(I) iodide (10 mol % based on aryl halide). The vessel was sealed with a rubber septum, evacuated, and backfilled with nitrogen (3×). A cosolvent of THF was added followed by the amine base. The terminal alkyne was then added followed by replacing the septum with a screw cap when a tube was used and the reaction was heated if necessary. TLC was used to follow the progress of the reaction, and when complete, the reaction vessel was cooled to room temperature. The mixture was quenched with water or a saturated solution of NH_4Cl. The organic layer was diluted with organic solvent and washed with brine (3×). The combined aqueous layers were extracted with organic solvent (3×), and the combined organic layers were dried over anhydrous $MgSO_4$. The slurry was filtered, and the solvent was removed from the filtrate in vacuo, followed by further purification of the residue as indicated.

4.3. General synthesis of *para*-disubstituted azobenzenes[7]

To a solution of the substituted aniline in CH_2Cl_2 was added Oxone® (2.00 equiv) dissolved in water. The mixture was stirred under nitrogen at room temperature until TLC monitoring indicated complete consumption of the starting material (2–24 h). The color of the solution generally turned to green as the corresponding nitrosoarene formed. After separation of the layers, the aqueous layer was extracted with

CH_2Cl_2 (3×). The combined organic layers were washed with 1 N HCl, saturated sodium bicarbonate solution, water, brine and dried with $MgSO_4$. After filtration, removal of the solvent from the filtrate in vacuo yielded the corresponding labile nitrosoarene, which was submitted to the next condensation step without further purification. To the nitrosoarene dissolved in acetic acid was added the substituted aniline (1.00 equiv). The resulting mixture was stirred at room temperature for 24–48 h. The precipitate was separated by filtration and the collected solid was washed with acetic acid and water and dried in a desiccator over P_2O_5 under reduced pressure. The compound was further purified by chromatography as necessary. For the acetic acid-soluble azobenzenes, saturated $NaHCO_3$ was added slowly to precipitate the product. The mixture was extracted with CH_2Cl_2 (3×). The combined extracts were dried with magnesium sulfate. After filtration the solvent was removed from the filtrate and the residue was chromatographed on silica gel.

4.3.1. (*E*)-2-(4-Iodophenyl)-1-phenyldiazene (12a). Following the general azobenzene synthesis procedure, a solution of nitrosobenzene **10a** (510 mg, 4.76 mmol) and 4-iodoaniline **11** (935 mg, 4.33 mmol) in acetic acid (30 mL) was stirred for 24 h. The product **12a** (1.13 g, 85%) was a yellow solid: mp 89–90 °C; FTIR (KBr) 3064, 1950, 1561, 1472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J=7.8, 1.7 Hz, 2H), 7.88 (d, J=8.4 Hz, 2H), 7.66 (d, J=8.4 Hz, 2H), 7.54–7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 152.2, 138.6 (2C), 131.6, 129.4 (2C), 124.7 (2C), 123.2 (2C), 97.9; HRMS calcd for $C_{12}H_9IN_2$ 307.9810, found 307.9805.

4.3.2. (*E*)-*S*-4-((4-(Phenyldiazenyl)phenyl)ethynyl)phenyl ethanethioate (1). Following the general coupling procedure, **12a** (259 mg, 0.841 mmol) was coupled to **13**[1] (163 mg, 0.925 mmol) using $PdCl_2(PPh_3)_2$ (23 mg, 0.034 mmol), CuI (13 mg, 0.067 mmol), TEA (1 mL), and THF (5 mL). Column chromatography of the crude product on silica gel (40% CH_2Cl_2 in hexanes) afforded **1** as a yellow solid (219 mg, 73%): mp 185–186 °C; FTIR (KBr) 3064, 2924, 2202, 1926, 1689, 1592, 1491, 1437, 1351, 1297, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 4H), 7.67 (d, J=8.4 Hz, 2H), 7.58 (d, J=8.1 Hz, 2H), 7.54–7.46 (m, 3H), 7.41 (d, J=8.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 152.6, 152.0, 134.3 (2C), 132.5 (2C), 132.2 (2C), 131.3, 129.1 (2C), 128.5, 125.5, 124.2, 123.0 (4C), 91.1, 90.8, 30.3; HRMS calcd for $C_{24}H_{24}N_2OS$ 356.0983, found 356.0972.

4.3.3. (*E*)-4-((4-(Phenyldiazenyl)phenyl)ethynyl)benzenethiol (2). A solution of ethanol (2 mL) and water (2 mL) was purged with N_2 for 40 min and then KOH (47 mg, 0.842 mmol) was added. The solution was purged again with N_2 for 20 min. The thioacetate **1** (90 mg, 0.252 mmol) was added and the solution was purged again with N_2 for 10 min. The reaction mixture was heated at reflux under N_2 for 30 min, and then was carefully neutralized with 1 N HCl under N_2. The orange solid was filtered, washed repeatedly with water under N_2 and dried in vacuo. Purification on silica gel using 40% CH_2Cl_2 in hexanes afforded the thiol **2** (48 mg, 61%) as an orange solid: mp 161–195 °C (broad range likely due to oxidative decomposition); FTIR (KBr) 3437, 3060, 2924, 2559, 2206, 1584, 1495, 1398, 1301 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 4H), 7.68 (d, J=8.6 Hz, 2H), 7.55–7.46 (m, 3H), 7.36 (d, J=8.4 Hz, 2H), 7.25 (d, J=8.4 Hz, 2H), 3.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.0, 132.6 (2C), 132.5 (2C), 132.4, 131.5, 129.4 (2C), 129.2 (2C), 126.1, 123.18 (2C), 123.17 (2C), 120.3, 91.6, 89.8; HRMS calcd for $C_{22}H_{22}N_2S$ 314.8777, found 314.8779.

4.3.4. (*E*)-1-(4-Iodophenyl)-2-(4-(trifluoromethyl)phenyl)diazene (12b). Following the general synthesis of azobenzenes procedure, to a solution of **9b** (1.50 g, 9.31 mmol) in CH_2Cl_2 (20 mL) was added a solution of Oxone® (11.5 g, 18.6 mmol) in H_2O (20 mL). The crude product (2.0 g) was dissolved in acetic acid (50 mL) and **11** (2.00 g, 9.31 mmol) was added. The resulting product **12b** was isolated as an orange solid (1.40 g, 40%): mp 150–151 °C; FTIR (KBr) 3076, 1942, 1577, 1476, 1336 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J=8.2 Hz, 2H), 7.91 (d, J=8.6 Hz, 2H), 7.79 (d, J=8.2 Hz, 2H), 7.69 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 151.9, 138.7 (2C), 132.7 (q, $^2J_{CF}$=32.5 Hz), 126.6 (2C, q, $^3J_{CF}$=3.7 Hz), 124.9 (2C), 124.1 (q, $^1J_{CF}$=272.4 Hz), 123.3 (2C), 99.0; HRMS calcd for $C_{13}H_8F_3IN_2$ 375.9682, found 375.9684.

4.3.5. (*E*)-*S*-4-((4-((4-(Trifluoromethyl)phenyl)diazenyl)phenyl)ethynyl)phenyl ethanethioate (3). Following the general coupling procedure, the iodoazobenzene **12b** (250 mg, 0.665 mmol) was coupled to **13** (129 mg, 0.731 mmol) using $PdCl_2(PPh_3)_2$ (19 mg, 0.027 mmol), CuI (10 mg, 0.053 mmol), TEA (1 mL), and THF (5 mL). The crude product was purified using column chromatography on silica gel (50% CH_2Cl_2 in hexanes) to afford **3** (201 mg, 71%) as an orange solid: mp 184–187 °C; FTIR (KBr) 3103, 2920, 2843, 2206, 1918, 1705, 1588, 1499, 1406, 1316 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J=8.2 Hz, 2H), 7.97 (d, J=8.7 Hz, 2H), 7.80 (d, J=8.2 Hz, 2H), 7.71 (d, J=8.7 Hz, 2H), 7.60 (d, J=8.5 Hz, 2H), 7.44 (d, J=8.5 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 154.6, 151.9, 134.5 (2C), 132.8 (2C), 132.5 (2C), 128.8, 126.7, 126.6 (2C, q, $^3J_{CF}$=3.8 Hz), 124.2, 124.1 (q, $^1J_{CF}$=272.4 Hz), 123.5 (2C), 123.3 (2C), 91.8, 90.8, 30.6 ($^2J_{CF}$ coupling of the aromatic carbon at the *ipso*-position from CF_3 group was not clearly observed due to the low intensity of the corresponding quartet signal); HRMS calcd for $C_{23}H_{15}F_3N_2OS$ 424.0857, found 424.0857.

4.3.6. (*E*)-4-((4-((4-(Trifluoromethyl)phenyl)diazenyl)phenyl)ethynyl)benzenethiol (4). A solution of ethanol (2 mL) and water (2 mL) was purged with N_2 for 30 min and KOH (66 mg, 1.2 mmol) was added. The solution was purged with N_2 for 20 min. The thioacetate **3** (90 mg, 0.236 mmol) was added and the solution was purged again with N_2 for 10 min. It was then heated at reflux under N_2 for 30 min. The reaction mixture was carefully neutralized with 1 N HCl under N_2. The yellow solid was filtered, washed repeatedly with water under N_2, and dried in a desiccator in vacuo to afford the thiol **4** (60 mg, 67%) as an orange solid: mp 184–187 °C; FTIR (KBr) 3289, 3044, 2919, 1953, 1736, 1605, 1443, 1301 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J=8.2 Hz, 2H), 7.96 (d, J=8.5 Hz, 2H), 7.80 (d, J=8.2 Hz, 2H), 7.68 (d, J=8.5 Hz, 2H), 7.44 (d, J=8.3 Hz, 2H), 7.27 (d, J=8.3 Hz, 2H), 3.56 (s, 1H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 154.6, 151.7, 132.8 (2C), 132.6, 132.5 (2C), 129.1 (2C), 127.0, 126.6 (2C, q, $^3J_{CF}$=3.8 Hz), 123.5 (2C), 123.3 (2C), 120.1, 92.2, 89.7; (Carbon signals with $^1J_{CF}$ and $^2J_{CF}$ couplings were not observed due to the low intensity of the quartet signals caused by limited solubility of the product.) HRMS calcd for $C_{21}H_{13}F_3N_2S$ 382.0753, found 382.0751.

4.3.7. (*E*)-1-(4-Iodophenyl)-2-(4-nitrophenyl)diazene (12c). Following the general procedure for synthesis of azobenzenes, to a solution of 4-nitroaniline **9c** (2.00 g, 14.5 mmol) in CH_2Cl_2 (40 mL) was added a solution of Oxone® (17.8 g, 29.0 mmol) in H_2O (150 mL). The crude intermediate was dissolved in acetic acid (50 mL) and then 4-iodoaniline (3.18 g, 14.5 mmol) was added. Purification of the product on silica gel (50% CH_2Cl_2 in hexanes) gave **12c** (2.60 g, 51%) as an orange solid containing a small amount of cis isomer (<5%) according to the ^{1}H NMR analysis: mp 237–243 °C; FTIR (KBr) 3099, 2928, 1926, 1596, 1515, 1468, 1332 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=9.1 Hz, 2H), 8.05 (d, J=9.1 Hz, 2H), 7.93 (d, J=8.7 Hz, 2H), 7.71 (d, J=8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 151.9, 149.1, 138.9 (2C), 125.1 (2C), 125.0 (2C), 123.8 (2C), 99.9; HRMS calcd for $C_{12}H_8IN_3O_2$ 352.9661, found 352.9664.

4.3.8. (*E*)-4-((4-((4-Nitrophenyl)diazenyl)phenyl)ethynyl)benzenethiol (5). Following the general coupling procedure, **12c** (96 mg, 0.26 mmol) was coupled to **13** (55 mg, 0.31 mmol) using $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol), CuI (8 mg, 0.042 mmol), TEA (1 mL), and THF (5 mL). Column chromatography of the crude product on silica gel (50% CH_2Cl_2 in hexanes) afforded **5** as an orange solid (66 mg, 62%): mp 184–185 °C; FTIR (KBr) 3103, 2924, 2854, 2214, 1709, 1522, 1491, 1340 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=8.9 Hz, 2H), 8.06 (d, J=8.9 Hz, 2H), 7.98 (d, J=8.5 Hz, 2H), 7.71 (d, J=8.5 Hz, 2H), 7.60 (d, J=8.3 Hz, 2H), 7.43 (d, J=8.3 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 155.9, 151.8, 149.1, 134.5 (2C), 132.9 (2C), 132.5 (2C), 129.0, 127.4, 125.0 (2C), 124.1, 123.8 (4C), 92.3, 90.7, 30.6; HRMS calcd for $C_{22}H_{15}N_3O_3S$ 401.0822, found 401.0834.

4.3.9. (*E*)-2-(4-(Phenyldiazenyl)phenyl)ethanol (15). Following the general azobenzene procedure, to a solution of aniline (1.05 g, 11.3 mmol) in CH_2Cl_2 (20 mL) was added a solution of Oxone® (13.9 g, 22.6 mmol) in H_2O (100 mL). The crude product was dissolved in acetic acid (100 mL) and 4-(hydroxyethyl)aniline (**14**) (1.55 g, 11.3 mmol) was added. After purification on silica gel (30% EtOAc in hexane), isolation of the product gave **15** (1.15 g, 44%) as an orange solid: mp 81–83 °C; FTIR (KBr) 3303, 3051, 2933, 2857, 1486, 1443, 1590, 1519, 1341 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.88 (m, 4H), 7.53–7.48 (m, 3H), 7.40 (d, J=8.5 Hz, 2H), 3.94 (t, J=6.5 Hz, 2H), 2.97 (t, J=6.5 Hz, 2H), 1.60 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 151.7, 142.2, 131.1, 130.0 (2C), 129.3 (2C), 123.3 (2C), 123.0 (2C), 63.7, 39.3; HRMS calcd for $C_{14}H_{14}N_2O$ 401.0822, found 401.0834.

4.3.10. (*E*)-1-(4-(2-(4-Bromobutoxy)ethyl)phenyl)-2-phenyldiazene (16). To a suspension of NaH (60% dispersion in mineral oil) in 7 mL of DMF was added dropwise at 0 °C the azobenzene ethanol **15** (600 mg, 2.65 mmol). NaI (40 mg, 0.26 mmol) and dibromobutane (2.30 g, 10.7 mmol) were then added to the solution. The reaction mixture was stirred for 32 h at room temperature. Since a significant amount of the starting alcohol was present in the mixture by TLC analysis, additional portions of NaH (212 mg, 5.30 mmol), dibromobutane (1.72 g, 7.96 mmol), and DMF (3 mL) were added to the solution. The reaction mixture was further stirred at room temperature for 20 h. Water was carefully added to quench the excess NaH after cooling the mixture to 0 °C. The aqueous layer was separated and extracted with CH_2Cl_2 (3×). The extracts were washed with brine, dried over $MgSO_4$, filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel. Elution with 10% EtOAc in hexanes gave the bromide **16** (352 mg, 36%) as an orange semi-solid: FTIR (KBr) 3049, 2932, 2850, 1950, 1600, 1478, 1433, 1347, 1243 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J=8.2 Hz, 2H), 7.87 (d, J=8.3 Hz, 2H), 7.53–7.47 (m, 3H), 7.38 (d, J=8.3 Hz, 2H), 3.69 (t, J=7.0 Hz, 2H), 3.49 (t, J=6.2 Hz, 2H), 3.43 (t, J=6.7 Hz, 2H), 2.97 (t, J=7.0 Hz, 2H), 1.94 (m, 2H), 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 151.5, 142.9, 131.0, 129.8 (2C), 129.3 (2C), 123.1 (2C), 123.0 (2C), 71.6, 70.2, 36.5, 34.0, 29.9, 28.4; HRMS calcd for $C_{18}H_{21}BrN_2O$ 360.0830, found 360.0837.

4.3.11. (*E*)-4-(4-(Phenyldiazenyl)phenethoxy)butane-1-thiol (6). A solution of the azobenzene bromide **16** (209 mg, 0.578 mmol) and thiourea (220 mg, 2.89 mmol) in ethanol (10 mL) was heated at reflux for 12 h. The solvent was evaporated under reduced pressure. To the concentrated mixture was added KOH (194 mg, 3.47 mmol) in nitrogen purged water (10 mL). The reaction mixture was heated at reflux for 1.5 h and then acidified with 1 N HCl. The aqueous mixture was extracted with CH_2Cl_2 (3×). The extracts were washed with brine, dried over $MgSO_4$, filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel. Elution with 20% EtOAc in hexanes gave the thiol **6** (127 mg, 70%) as an orange solid: mp 31–33 °C; FTIR (KBr) 3425, 3054, 2947, 2851, 2794, 2558, 1955, 1598, 1480, 1434, 1366, 1302 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.85 (d, J=8.4 Hz, 2H), 7.52–7.42 (m, 3H), 7.36 (d, J=8.4 Hz, 2H), 3.65 (t, J=7.0 Hz, 2H), 3.43 (t, J=5.7 Hz, 2H), 2.94 (t, J=7.0 Hz, 2H), 2.51 (m, 2H), 1.64 (m, 4H), 1.32 (t, J=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.7, 143.1, 131.0, 130.1 (2C), 129.5 (2C), 123.6 (2C), 123.3 (2C), 71.8, 70.8, 36.7, 31.0, 28.8, 24.9; HRMS calcd for $C_{18}H_{22}N_2OS$ 314.1449, found 314.1453.

4.3.12. (*E*)-4-((4-(Trifluoromethyl)phenyl)diazenyl)benzeneamine (18). Following the general azobenzene procedure, to a solution of **9b** (1.50 g, 9.31 mmol) in CH_2Cl_2 (20 mL) was added a solution of Oxone® (11.5 g, 18.6 mmol) in H_2O (20 mL). The crude product was dissolved in acetic acid (60 mL) and *p*-phenylenediamine (**17**) (1.00 g, 9.31 mmol) was added. After workup, the crude product was purified on silica gel using CH_2Cl_2 to give **18** (1.05 g, 43%) as an orange solid: mp 134–136 °C; FTIR (KBr) 3503, 3410, 3056, 2920, 1938, 1592, 1499, 1425, 1394, 1316, 1289 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 7.92 (d, J=9.0 Hz, 2H), 7.81 (d, J=9.0 Hz, 2H), 7.77 (d, J=8.8 Hz, 2H), 6.76 (d, J=8.8 Hz, 2H), 4.96 (br s, 2H);

^{13}C NMR (125 MHz, CD_3CN) δ 156.5, 154.1, 145.6, 131.3 (q, $^2J_{CF}$=32.1 Hz), 127.7 (2C, q, $^3J_{CF}$=3.9 Hz), 127.0 (2C), 125.7 (q, $^1J_{CF}$=271.1 Hz), 123.7 (2C), 115.3 (2C); HRMS calcd for $C_{13}H_{10}F_3N_3$ 265.0827, found 265.0824.

4.3.13. (*E*)-4-((4-(Trifluoromethyl)phenyl)diazenyl)benzendiazonium tetrafluoroborate (7). In a 100 mL round-bottom flask was placed boron trifluoride-diethyl etherate (0.143 mL, 1.13 mmol). The flask was submerged into a dry ice bath to control the temperature at −40 °C. The diazobenzeneamine **18** (100 mg, 0.377 mmol) in THF (4 mL) was added dropwise. The reaction mixture was stirred for 10 min and then *tert*-butylnitrite (0.090 mL, 0.75 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the solid washed with excess ether to afford the diazonium salt **7** (130 mg, 95%): FTIR (KBr) 3363, 3212, 3107, 2291, 1938, 1802, 1577, 1475, 1456, 1332 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.13 (d, *J*=9.1 Hz, 2H), 8.51 (d, *J*=9.1 Hz, 2H), 8.26 (d, *J*=8.2 Hz, 2H), 8.06 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (125 MHz, acetone-d_6) δ 159.2, 155.1, 135.9 (2C), 134.6 (q, $^2J_{CF}$=32.6 Hz), 127.8 (2C, q, $^3J_{CF}$=3.8 Hz), 126.1 (2C), 125.2 (2C), 124.8 (q, $^1J_{CF}$=271.8 Hz), 117.8.

4.3.14. (*E*)-1-(4-Nitrophenyl)-2-(4-tritylphenyl)diazene (22). Following the general azobenzene procedure, to a solution of **19** (1.00 g, 7.24 mmol) in CH_2Cl_2 (20 mL) was added a solution of Oxone® (8.90 g, 14.5 mmol) in H_2O (80 mL). After workup, the crude product was dissolved in acetic acid (50 mL) and 4-tritylaniline **21** (2.43 g, 7.24 mmol) was added to give a product that was recrystallized from hexanes to afford **22** (2.79 g, 82%) as an orange solid: mp 301–302 °C; FTIR (KBr) 3052, 2443, 1957, 1592, 1515, 1492, 1437, 1350, 1312 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J*=9.1 Hz, 2H), 8.01 (d, *J*=9.1 Hz, 2H), 7.87 (d, *J*=8.8 Hz, 2H), 7.46 (d, *J*=8.8 Hz, 2H), 7.30–7.23 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 152.1, 150.6, 148.9, 146.4 (3C), 132.3 (2C), 131.3 (6C), 128.0 (6C), 126.4 (3C), 125.0 (2C), 123.6 (2C), 122.8 (2C), 65.4; HRMS calcd for $C_{31}H_{23}N_3O_2$ 469.1787, found 469.1790.

4.3.15. (*E*)-4-((4-Tritylphenyl)diazenyl)benzeneamine (23). To **22** (1.50 g, 3.19 mmol) in a solution of dioxane (80 mL), ethanol (20 mL), and water (5 mL) was added sodium sulfide (2.30 g, 9.58 mmol). The mixture was heated at 80 °C for 1.5 h. The solvents were partly evaporated and the residue was dissolved in CH_2Cl_2. The solution was washed with 1 N HCl followed by saturated $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel using 60% CH_2Cl_2 in hexanes to give **23** (1.14 g, 81%): mp 230–231 °C; FTIR (KBr) 3476, 3379, 3056, 3025, 1957, 1619, 1503, 1445, 1417, 1289 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J*=8.7 Hz, 2H), 7.73 (d, *J*=8.7 Hz, 2H), 7.36 (d, *J*=8.7 Hz, 2H), 7.30–7.20 (m, 15H), 6.75 (d, *J*=8.7 Hz, 2H), 4.11 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 149.8, 148.9, 146.7 (3C), 145.8, 132.0 (2C), 131.3 (6C), 127.8 (6C), 126.2 (3C), 125.3 (2C), 121.5 (2C), 114.9 (2C), 65.2; HRMS calcd for $C_{31}H_{25}N_3$ 439.2048, found 439.2048.

4.3.16. (*E*)-4-((4-Tritylphenyl)diazenyl)benzendiazonium tetrafluoroborate (8). In a 100 mL round-bottom flask was placed boron trifluoride-diethyl etherate (0.432 mL, 3.41 mmol). The flask was submerged into a dry ice bath to control the temperature at −40 °C. The diazobenzeneamine **23** (500 mg, 1.14 mmol) in THF (15 mL) was added dropwise. The reaction mixture was stirred for 10 min and then *tert*-butylnitrite (0.273 mL, 2.28 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the solid was washed with excess ether to afford the pure diazonium salt **8** (520 mg, 85%): FTIR (KBr) 3348, 3111, 3045, 2272, 1957, 1817, 1577, 1487, 1413, 1317 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J*=8.2 Hz, 2H), 8.29 (d, *J*=8.2 Hz, 2H), 7.99 (d, *J*=7.5 Hz, 2H), 7.65 (d, *J*=7.5 Hz, 2H), 7.42–7.33 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.3, 150.9, 146.8 (3C), 135.0 (2C), 132.6 (2C), 131.2 (6C), 128.5 (6C), 126.8 (3C), 125.6 (2C), 123.8 (2C), 114.9, 65.9.

4.3.17. (*E*)-1-(4-Bromophenyl)-2-phenyldiazene (24).[14] Following the general azobenzene procedure, to a solution of 4-bromoaniline (2.50 g, 14.9 mmol) in CH_2Cl_2 (45 mL) was added a solution of Oxone® (17.9 g, 29.8 mmol) in H_2O (180 mL). The crude product (2.78 g) was >90% pure by ^{1}H NMR. A portion (500 mg, 2.70 mmol) was dissolved in acetic acid (30 mL) and was condensed with aniline (210 mg, 2.25 mmol). Purification on silica gel using 5% CH_2Cl_2 in hexanes gave the **24** (520 mg, 74%) as an orange solid: mp 89–90 °C; FTIR (KBr) 3084, 1573, 1480 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J*=8.1 Hz, 2H), 7.80 (d, *J*=8.5 Hz, 2H), 7.65 (d, *J*=8.5 Hz, 2H), 7.55–7.47 (m, 3H).

4.3.18. (*E*)-1-(4-Bromophenyl)-2-(4-iodophenyl)diazene (25). A portion of the crude 4-bromonitrosobenzene (500 mg, 2.70 mmol) from the preparation of **24** was dissolved in acetic acid (30 mL) and **11** (493 mg, 2.25 mmol) was added. Workup provided **25** (810 mg, 93%) as an orange solid: mp 209–212 °C; FTIR (KBr) 3068, 1907, 1561, 1472, 1394, 1336 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=8.7 Hz, 2H), 7.80 (d, *J*=8.8 Hz, 2H), 7.66 (d, *J*=8.8 Hz, 2H), 7.65 (d, *J*=8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 151.4, 138.7 (2C), 132.6 (2C), 126.0, 124.74 (2C), 124.67 (2C), 98.3; HRMS calcd for $C_{12}H_8BrIN_2$ 385.8916, found 385.8915.

4.3.19. (*E*)-1-(4-Iodophenyl)-2-(4-((trimethylsilyl)ethynyl)phenyl)diazene (26). Following the general azobenzene procedure, to a solution of 4-((trimethylsilyl)ethynyl)aniline[15] (250 mg, 1.32 mmol) in CH_2Cl_2 (2.5 mL) was added a solution of Oxone® (1.63 g, 2.62 mmol) in H_2O (20 mL). The crude product was dissolved in acetic acid (20 mL) and **11** (289 mg, 1.32 mmol) was added. Workup and chromatography using 5% CH_2Cl_2 in hexane on silica gel gave **26** (185 mg, 35%) as an orange solid: mp 143–144 °C; FTIR (KBr) 2948, 2155, 1926, 1565, 1468, 1398, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=8.7 Hz, 2H), 7.87 (d, *J*=8.7 Hz, 2H), 7.66 (d, *J*=8.7 Hz, 2H), 7.61 (d, *J*=8.7 Hz, 2H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 151.9, 138.6 (2C), 133.1 (2C), 126.4, 124.7 (2C), 123.1 (2C), 104.8, 98.3, 97.6, 0.1 (3C); HRMS calcd for $C_{17}H_{17}IN_2Si$ 404.0213, found 404.0206.

4.3.20. (*E*)-2-(4-((4-Nitrophenyl)diazenyl)phenyl)ethanol (27). Following the general azobenzene procedure, to a solution of 4-nitroaniline (**19**) (1.20 g, 8.69 mmol) in CH_2Cl_2 (20 mL) was added a solution of Oxone® (10.7 g, 17.4 mmol) in H_2O (80 mL). The crude product was dissolved in acetic acid (150 mL) and 4-(hydroxyethyl)aniline (**14**) (1.90 g, 8.69 mmol) was added. After workup the residue was chromatographed on silica gel using 30% EtOAc in hexane to give **27** (1.69 g, 72%) as an orange solid: mp 149–152 °C; FTIR (KBr) 3522, 3402, 3103, 2940, 1915, 1653, 1584, 1522, 1495, 1340, 1207, 1099, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J=9.1 Hz, 2H), 8.03 (d, J=9.1 Hz, 2H), 7.94 (d, J=8.4 Hz, 2H), 7.44 (d, J=8.4 Hz, 2H), 3.96 (t, J=6.5 Hz, 2H), 2.99 (t, J=6.5 Hz, 2H), 1.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 151.4, 148.8, 144.0, 130.2 (2C), 124.9 (2C), 123.9 (2C), 123.6 (2C), 63.5, 39.3; HRMS calcd for $C_{14}H_{13}N_3O_3$ 271.0959, found 271.0957.

Acknowledgements

We thank DARPA and the AFOSR for funding this research. B.-C.Y. thanks Mokwon University for funding during sabbatical leave in 2005.

References and notes

1. Tour, J. M. *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming*; World Scientific: River Edge, NJ, 2003.
2. (a) Hwang, J.-J.; Tour, J. M. *Tetrahedron* **2002**, *58*, 10387–10405; (b) Dirk, S. M.; Tour, J. M. *Tetrahedron* **2003**, *59*, 287–293; (c) Price, D. W.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497–2518; (d) Price, D. W., Jr.; Tour, J. M. *Tetrahedron* **2003**, *59*, 3131–3156; (e) Flatt, A. K.; Dirk, S. D.; Henderson, J. C.; Shen, D. E.; Su, J.; Reed, M. A.; Tour, J. M. *Tetrahedron* **2003**, *59*, 8555–8570; (f) Dameron, A. A.; Ciszek, J. W.; Tour, J. M.; Weiss, P. S. *J. Phys. Chem. B* **2004**, *108*, 16761–16767; (g) Lewis, P. A.; Inman, C. E.; Maya, F.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 17421–17426; (h) Choi, B.-Y.; Kahng, S.-J.; Kim, S.; Kim, H.; Kim, H. W.; Song, Y. J.; Ihm, J.; Kuk, Y. *Phys. Rev. Lett.* **2006**, *96*, 156106-1–156106-4.
3. Astrand, P. O.; Ramanujam, P. S.; Hvilsted, S.; Bak, K.; Sauer Stephan, P. A. *J. Am. Chem. Soc.* **2000**, *122*, 3482–3487.
4. (a) Evans, S. D.; Johnson, S. R.; Ringsdorf, H.; Williams, L. M.; Wolf, H. *Langmuir* **1998**, *14*, 6436–6440; (b) Stiller, B.; Knochenhauer, G.; Markava, E.; Gustina, D.; Muzikante, I.; Karageorgiev, P.; Brehmer, L. *Mater. Sci. Eng.* **1999**, *C8-9*, 385–389; (c) Landraud, N.; Peretti, J.; Chaput, F.; Lampel, G.; Boilot, J.-P.; Lahlil, K.; Safarov, V. *Appl. Phys. Lett.* **2001**, *79*, 4562–4564; (d) Matsumoto, M.; Miyazaki, D.; Tanaka, M.; Azumi, R.; Manda, E.; Kondo, Y.; Yoshino, N.; Tachibana, H. *J. Am. Chem. Soc.* **1998**, *120*, 1479–1484; (e) Tamada, K.; Akiyama, H.; Wei, X. *Langmuir* **2002**, *18*, 5239–5246; (f) Jaschke, M.; Schonherr, H.; Wolf, H.; Butt, H. J.; Bamberg, E.; Besocke, M. K.; Ringsdorf, H. *J. Phys. Chem.* **1996**, *100*, 2290–2301; (g) Ichimura, K.; Oh, S.-K.; Nakagawa, M. *Science* **2000**, *288*, 1624–1626; (h) Hugel, T.; Bolland, N.; Cattani, A.; Moroder, L.; Sitz, M.; Gaub, H. *Science* **2002**, *296*, 1103–1106; (i) Kajikawa, K.; Anzai, T.; Takezoe, H.; Fukuda, A. *Thin Solid Films* **1994**, *243*, 587–591.
5. Yasuda, S.; Nakamura, T.; Matsumoto, M.; Shigekawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 16430–16433.
6. Stewart, M. P.; Maya, F.; Kosynkin, D. V.; Dirk, S. M.; Stapleton, J. J.; McGuiness, C. L.; Allara, D. L.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 370–378.
7. Priewisch, B.; Rück-Braun, K. *J. Org. Chem.* **2005**, *70*, 2350–2352.
8. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470.
9. Akiyama, H.; Tamada, K.; Nagasawa, J.; Abe, K.; Tamaki, T. *J. Phys. Chem. B* **2003**, *107*, 130–135.
10. (a) Maya, F.; Chanteau, S. H.; Cheng, L.; Stewart, M. P.; Tour, J. M. *Chem. Mater.* **2005**, *17*, 1331–1345; (b) Radugc, C.; Papastavrou, D. G.; Kurth, D. G.; Motschmann, H. *Eur. Phys. J. E* **2003**, *10*, 103–114; (c) Vanoppen, P.; Grim, P. C. M.; Rücker, M.; De Feyter, M. S.; Moessner, G.; Valiyaveettil, S.; Müllen, K.; De Schryver, F. C. *J. Phys. Chem.* **1996**, *100*, 19636–19641; (d) Matsumoto, K.; Kubota, M.; Matsuoka, H.; Yamaoka, H. *Macromolecules* **1999**, *32*, 7122–7127.
11. (a) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271–1308; (b) Delorme, N.; Bardeau, J.-F.; Bulou, A.; Poncin-Epaillard, F. *Langmuir* **2005**, *21*, 12278–12282; (c) He, J.; Chen, B.; Flatt, A. K.; Stephenson, J. J.; Doyle, C. D.; Tour, J. M. *Nat. Mater.* **2006**, *5*, 63–68.
12. Matsui, M. *J. Fluorine Chem.* **1999**, *96*, 65–69.
13. Humphrey, J.; Lott, K. M.; Wright, M. E.; Kuciauskas, D. *J. Phys. Chem. B* **2005**, *109*, 21496–21498.
14. Denonne, F.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **2003**, *86*, 3096–3117.
15. Chang, J. Y.; Rhee, S. B.; Cheong, S.; Yoon, M. *Macromolecules* **1992**, *25*, 2666–2670.