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Phenylene Ethynylene Diazonium Salts as Potential Self-Assembling Molecular Devices

Dmitry V. Kosynkin and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main Street, Houston, Texas 77005

tour@rice.edu

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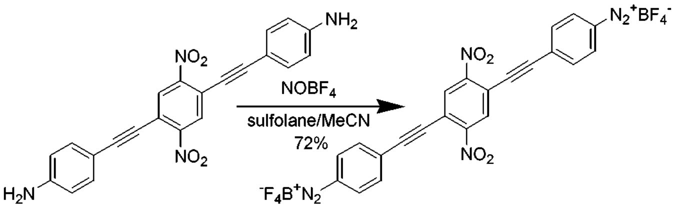
ABSTRACT



Functionalized diazonium salts for molecular electronic devices are prepared by the reaction of the corresponding anilines with NOBF$_4$ in sulfolane–acetonitrile solvent.

A large number of conjugated aromatic molecules have recently been synthesized as potential switches, wires, controllers, and gates of a molecular computer.[1] Favorable nonlinear conductive properties, including negative differential resistance (NDR), have been observed in several molecular devices.[2] However, making molecular electronic components an alternative to the presently utlilized silicon analogues will demand reliable methods of low impedance attachment of the molecules to conductive leads. Hence, our study is directed toward the organic molecule/metal interface impedance minimization.

While the interface conductance is expected to drop exponentially as the distance between the conjugated π-system of the molecular electronic device and the metal surface increases,[3] the “alligator clip” most widely used to attach molecular wires to metal substrates, the thiol group,[4] unavoidably introduces an extra atom and a covalent bond into the molecule-to-metal gap. In an attempt to alleviate this problem, we utilized the well-established reactivity of aromatic diazonium salts toward transition metals[5] that could produce a direct connection of the organic molecules to metal surfaces through a carbon−metal bond.

An important issue that had to be addressed during the design of the diazonium-terminated molecular devices was the potentially poor solubility of this class of rigid rod diazonium salts.[5] Fortunately, the introduction of ethyl or nitro groups into the phenylene moieties of the diazonium tetrafluoroborates resulted in at least 10 mg/mL solubilities in acetonitrile, thereby more than sufficient for subsequent chemisorption studies. In addition to the more convenient handling of the diazonium salts, the strongly electron-withdrawing nitro substituents were anticipated to impart

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(1) (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791. (b) Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L.; Tour, J. M. *Appl. Phys. Lett.* **1997**, *71*, 611.

(2) (a) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J. Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172. (b) Collier, C. P.; Wong, E. W.; Belohradský, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391. (c) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.

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(4) (a) Creager, S.; Yu, C. J.; Bamdad, C.; Oconnor, S.; Maclean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J. Y.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059. (b) Vondrak, T.; Cramer, C. J.; Zhu, X. −Y. *J. Phys. Chem.* **1999**, *103*, 8915. (c) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh. A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

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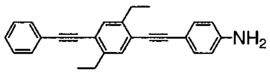
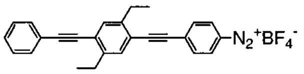
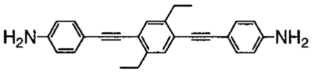
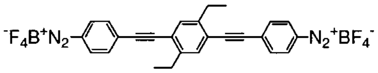
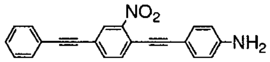
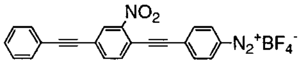
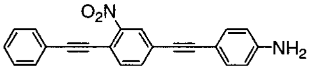
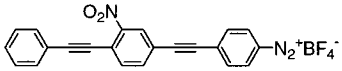
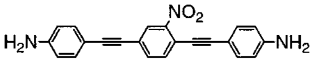
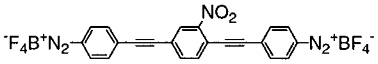
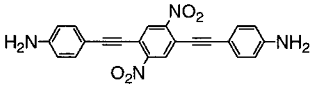
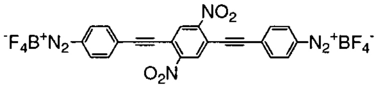
Table 1. Comparison of Diazotization in Pure Acetonitrile and Acetonitrile−Sulfolane Mixture

entry	starting aniline	product	yield (%)[a]	
			CH_3CN	CH_3CN - sulfolane
1	 **1**	 **7**	94	84
2	 **2**	 **8**	80	92
3	 **3**	 **9**	54[b]	81
4	 **4**	 **10**	51[b]	77
5	 **5**	 **11**	0	73
6	 **6**	 **12**	0	72

[a] Recrystallized salt. [b] Impure product.

useful electron storage or switching properties to their cores, as well as reducing the LUMO energies and thereby improving their electrical conductance.[1,2,6]

Among the plethora of methods previously reported for the conversion of anilines to the corresponding diazonium salts, none have proven universally suitable for the oligo(phenylene ethynylene)anilines. Aqueous acidic conditions were found to destroy the triple bonds, diazotization in acetonitrile or its mixtures with dichloromethane gave products contaminated with inseparable impurities in the case of nitro substituted amines, and the alkyl nitrite/boron trifluoride etherate treatment according to Doyle and Bryker[7] also met with little success. A likely explanation for the poor ability of known techniques to convert the nitro-substituted oligo(phenylene ethynylene)anilines into the corresponding diazonium salts resides with the very low solubility of these materials in the usual organic solvents.

The structural similarity of sulfolane to THF, which is effective at the dissolution of the other oligo(phenylene ethynylene)s, combined with its stability to electrophilic attack[8] encouraged us to evaluate the utility of this solvent for our reactions. The high melting point of sulfolane (29 °C) required the addition of 50% (v/v) acetonitrile to make the media suitable for the formation of the thermally unstable diazonium salts.[9] As Table 1 indicates, unlike acetonitrile alone the sulfolane/acetonitrile system afforded salts **7**−**12** in very good yields. Even diamine **6**, with its extremely poorly solubility, produced the diazonium salt in 72% yield.

The diazotization was typically accomplished by dropwise addition of a solution of the oligo(phenylene ethynylene)aniline (0.25 mmol) in sulfolane (1.5 mL) and acetonitrile (0.5 mL) to a suspension of finely dispersed nitrosonium tetrafluoroborate[10] in sulfolane (0.5 mL) and acetonitrile (1.5 mL) at −40 to −30 °C. After the complete disappearance of the color characteristic of the aniline (typically 30 min), the reaction mixture was allowed to reach 0 °C and then treated with dry ether or dichloromethane to precipitate the desired diazonium salt (CAUTION!).[11]

All of the oligo(phenylene ethynylene)anilines described here were synthesized from commercially available starting materials via multiple Sonogashira[12] couplings as illustrated for aniline **1** (Scheme 1).

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(6) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224.

(7) Doyle, M. P.; Bryker, J. W. *J. Org. Chem.* **1979**, *44*, 1572.

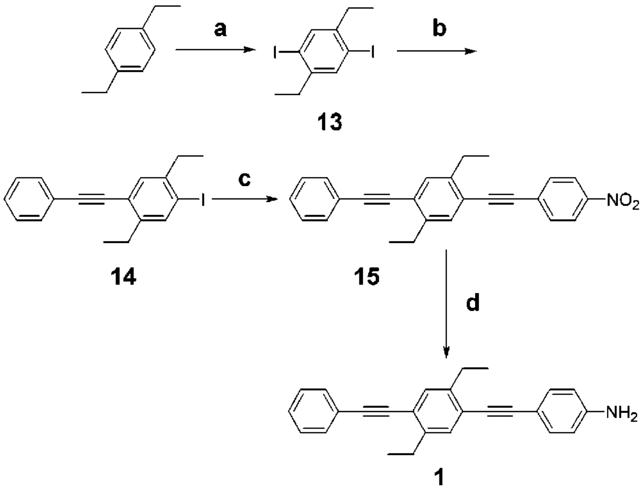
(8) Olah, G. A.; Laali, K.; Farooq, O.; Olah, J. A. *J. Org. Chem.* **1990**, *55*, 5179.

(9) To maximize the solubility of the starting amines, a mixture of sulfolane with only 10−25% acetonitrile was used for their dissolution, while the nitrosonium tetrafluoroborate was suspended in a lower freezing mixture of sulfolane with 75−90% acetonitrile.

(10) Kosynkin, D.; Bockman, T. M.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2003. (b) Kosynkin, D.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 4846. Commercial samples of $NOBF_4$ give more byproducts.

(11) *CAUTION!* All dry diazonium salts reported in this study displayed considerable DSC exotherms above 100−120 °C and should be handled as potentially explosive materials. Oligo(phenylene ethynylene)diazonium tetrafluoroborates are moderately light sensitive and should be stored in a freezer in the dark to avoid decomposition.

Scheme 1[a]

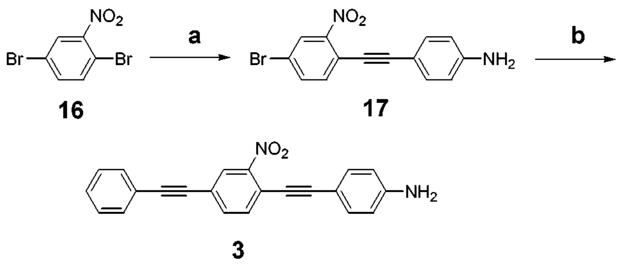


[a] (a) I_2, H_5IO_6, AcOH, H_2SO_4, 100 °C, 56%; (b) ethynylbenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 38%; (c) 1-ethynyl-4-nitrobenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 99%; (d) $SnCl_2{\cdot}2H_2O$, THF, EtOH, 97%.

The nitro derivative **15** and the structurally similar bis-nitro precursor of the diamine **2** were poorly soluble in alcohols routinely used as a reaction medium for tin(II) reduction of aromatic nitro compounds to anilines. Fortunately, the use of THF as a solvent brought about rapid and selective formation of the desired amines.

Evidently, this efficient formation of terminal amino groups from the nitro precursors was no longer feasible for the molecules bearing nitro groups on the central ring of the conjugated π-system. In this case, the terminal amino group was introduced through the coupling with 4-ethynylaniline (Scheme 2).

Scheme 2[a]



(a) 4-Ethynylaniline, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 49%; (b) ethynylbenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 97%.

The moderate yield of aniline **17** apparently resulted from the concomitant formation of the bis-alkynylated product **5** along with the undesirable mono-alkynylated isomer. Although more selective approaches to **17** can very easily be envisioned, the present one offers the valuable advantage of being concise.

In conclusion, we have synthesized a novel class of aromatic diazonium salts. In addition, a diazotization procedure suitable for poorly soluble anilines was developed. Studies involving the modification of conductive surfaces with the diazonium-terminated molecular devices are currently in progress.

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Supporting Information Available: ^1H NMR, ^{13}C NMR, IR, and mass spectroscopy for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron. Lett.* **1975**, 4467. (b) Takahashi, S.; Hagihara, N.; Kuroyama, Y; Sonogashira, K. *Synthesis* **1980,** 627.