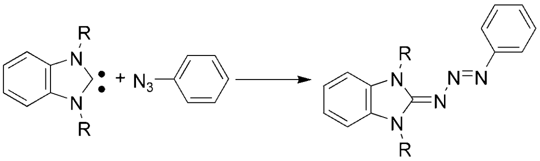
DOI: 10.1002/ange.200901046

Adapting N-Heterocyclic Carbene/Azide Coupling Chemistry for Polymer Synthesis: Enabling Access to Aromatic Polytriazenes**

*Daniel J. Coady, Dimitri M. Khramov, Brent C. Norris, Andrew G. Tennyson, and Christopher W. Bielawski**

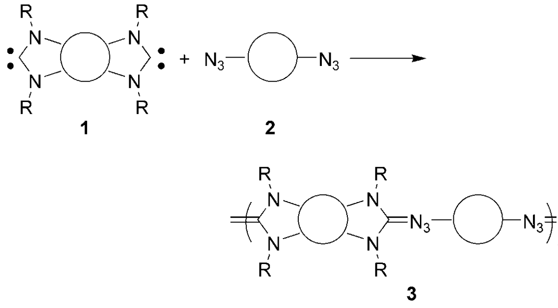
Aromatic polymers containing carbon–nitrogen double bonds, such as poly(azine)s and poly(azomethine)s,[1] have garnered tremendous interest across a range of scientific and engineering disciplines.[2] These polymers commonly exhibit high thermal stabilities[3] as well as good mechanical[4] and electronic properties,[3,5] including nonlinear optical[6] and semiconductive characteristics upon doping,[7] making them good candidates for use in a variety of optoelectronic applications. Since they can also coordinate to a variety of transition metals and other electrophilic species, aromatic polymers containing $C{=}N$ bonds are well-suited for applications ranging from catalysis to sensing.[8] In general, such polymers are prepared by condensation polymerizations involving difunctional monomers (typically, bisaldehydes and bisamines), although the high reactivity between primary amines and aldehydes often renders the polymerization reaction uncontrollable, resulting in the formation of intractable products.[1,3,4] As a result, there is a need for the development of new polymerization methods for forming the aforementioned types of aromatic polymeric materials,[9] particularly those that offer a broad range of options for varying the structures as well as the functionalities of the polymers produced.

Recently, we reported a new method for forming $C{=}N$ bonds which involves the combination of N-heterocyclic carbenes (NHCs)[10] with organic azides to afford the respective acyclic triazenes [Eq. (1)].[11] The reaction tolerates a wide variety of both NHC and azide coupling partners, and proceeds in high yields. Through a comprehensive product analysis, we determined that the electronic delocalization across the triazeno linkage was efficient and could be tuned by varying the nature of the coupling partners.[11,12] Furthermore, despite their relatively high nitrogen atom contents, the triazene products are thermally stable. For example, derivatives possessing bulky N-substituents (e.g., *tert*-butyl) were found to be stable in the solid state at temperatures exceeding 150 °C.[11]



(1)

Collectively, the unique features of the NHC/azide coupling reaction is well suited for use in synthetic polymer chemistry,[13] particularly for accessing aromatic polymers containing $C{=}N$ bonds. We envisioned combining difunctional NHCs (**1**) with complementary difunctional azides (**2**) to create a new class of aromatic polymers (**3**) [Eq. (2); ○ = arene linker].[14] As a corollary to this investigation, we sought to expand the utility of organic azides as building blocks in synthetic polymer chemistry. Although metal-catalyzed "click" cycloaddition reactions[15] have found tremendous utility in such regards,[16] one important advantage of the NHC/azide coupling chemistry is that it does not require a catalyst, thereby facilitating the isolation of pure materials.



(2)

The structures of the various bis(NHC)s **1** and bis(azide)s **2** that were investigated as potential monomers are shown in Figure 1. The bis(NHC)s were prepared from their respective tetraamines and subsequent formylative cyclization and deprotonation, in accord with published procedures.[17] The N-substituents featured in these monomers were chosen to enhance the solubilities of the respective polymers as well as to probe their effects on the thermal and electronic properties displayed by these materials (see below).[18] To maximize the formation of polymers with electronically delocalized structures, aryl bis(azide)s were studied exclusively. In particular, 1,4-diazidobenzene (**2a**) as well as 4,4′-diazidobiphenyl (**2b**) were synthesized. Considering that polymers containing fluorene have been used in display devices,[19] the 2,7-diazido derivative **2c**, featuring two *n*-hexyl chains at the 9-position to enhance photostability and solubility, was also studied.

---

[*] Dr. D. J. Coady, Dr. D. M. Khramov, B. C. Norris, Dr. A. G. Tennyson, Prof. C. W. Bielawski
Department of Chemistry & Biochemistry
The University of Texas at Austin, Austin, TX 78712 (USA)
E-mail: bielawski@cm.utexas.edu

[**] We are grateful to the NSF (CHE-0645563), the ARO (W911NF-05-1-0430), the ONR (N00014-08-1-0729), the Robert A. Welch Foundation (F-1621), the Arnold and Mabel Beckman Foundation, and the Research Corporation for their generous financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901046.

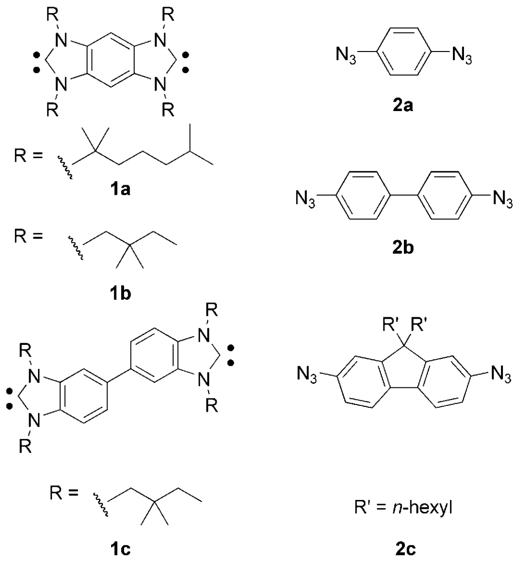


Figure 1. Structures of the bis(NHC)s **1** and bis(azide)s **2** explored in this study.

In an initial experiment, the bis(NHC) **1a** was added to an equimolar quantity of bis(azide) **2a** in CD_2Cl_2 ([total monomer]$_0 = 0.1$ M) and then stirred at 25 °C. Gratifyingly, the expected polymer **3a** was observed by ^{1}H NMR spectroscopy (through development of broad signals that were shifted downfield) shortly after the monomers were combined. Polymer formation was monitored over time by integrating signals diagnostic of the monomer **2a** ($\delta = 7.00$ ppm) to its analogous signals found in the repeat units of **3a** ($\delta = 7.58$ ppm). Furthermore, by comparing signals attributed to the end groups of **3a** (terminal triazene Ar$-H$, $\delta = 7.05$ ppm) to the signals associated with its main chain, the number-average molecular weight ($\bar{M}_n$)of the polymer was calculated. After 24 hours, the reaction appeared to be complete, producing a polymer having a $\bar{M}_n = 29.4$ kDa.[20] The reaction mixture was then poured into an excess of *n*-pentane, a poor solvent for the polymer but a good solvent for its composite monomers. The precipitated solids were collected and then dried under high vacuum to afford **3a** in 98 % yield. Analysis of the polymer by gel permeation chromatography (GPC) revealed an absolute $\bar{M}_n = 31.8$ kDa and a broad polydispersity (PDI = 1.8),[21] as expected for a step-growth polymerization (Figure 2 a). As a testament to its high purity, the elemental composition of **3a** (C, 72.95; H, 10.04; N, 17.01) was found to be in good agreement with its calculated values (C, 72.67; H, 10.24; N 17.09).

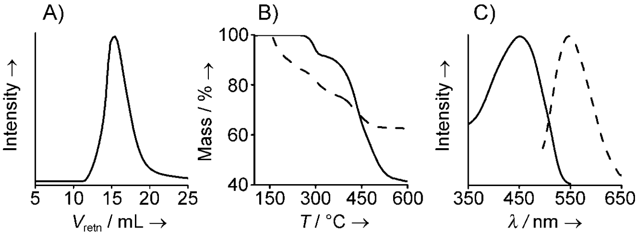


Figure 2. A) Gel permeation chromatogram of **3a**. Conditions: 40 °C, THF/pyridine (3:1) as eluent, 1 mL min^{-1}. B) Thermogravigrams of **3a** (dotted line) and **3g** (solid line). Conditions: 10 °C min^{-1}, nitrogen atmosphere. C) Normalized absorption (solid line) and emission (dashed line) spectra for **3c** in THF at 25 °C.

Table 1: Key properties of the polytriazenes prepared from the monomers indicated.[a]

Polymer	Yield [%][b]	$\bar{M}_{n,\mathrm{NMR}}$ [kDa][c]	$\bar{M}_{n,\mathrm{GPC}}$ [kDa][d]	PDI	T_d [°C][e]	λ_{max} [nm][f]
3a (**1a** + **2a**)	98	29.4	34.8	1.8	154	485
3b (**1a** + **2b**)	95	24.6	27.5	1.6	157	434
3c (**1a** + **2c**)	76	21.5	23.9	1.8	160	450
3d (**1b** + **2c**)	81	8.3	17.6	1.6	262	476
3e (**1c** + **2a**)	96	22.1	27.6	2.3	282	437
3f (**1c** + **2b**)	95	20.3	22.7	2.3	282	379
3g (**1c** + **2c**)	72	17.7	19.9	1.9	278	436

[a] All polymerization reactions were performed in either tetrahydrofuran or dichloromethane using equimolar quantities of monomers **1** and **2** (total initial concentration of monomer = 0.1 M). [b] Yields of isolated polymeric products obtained after precipitation in *n*-pentane. Polymers containing **2c** were partially soluble in *n*-pentane, which resulted in lower yields of the isolated polymer. Monomer conversion into polymer, as determined by ^{1}H NMR spectroscopy, was quantitative. [c] Determined by end-group analysis (see text). [d] Performed using THF/pyridine (9:1) as the eluent at 40 °C using light scattering, refractive index, and viscometry detectors. [e] Performed under an atmosphere of nitrogen at a scan rate of 10 °C min^{-1}. [f] UV/Vis spectra were recorded in THF at 25 °C.

As summarized in Table 1, a series of analogous polymerizations were performed using various combinations of bis(NHC)s **1** and bis(azide)s **2**. Each of these reactions were performed on a preparative scale in THF or CH_2Cl_2 for 24 hours, after which the reaction mixture was poured into *n*-pentane, quenching the reaction and causing the respective polymers to precipitate. The structures of the polytriazenes obtained from these reactions were confirmed by NMR spectroscopy. Their NMR-derived $\bar{M}_n$ values ranged from 8.3 to 29.4 kDa and compared well to those obtained by GPC methods. In general, polymerizations involving **1a** produced higher molecular weight (MW) polymers than analogous reactions involving **1c**.[22] The difference may be explained by the reduced conformational freedom associated with the former monomers, thus reducing chances for molecular weight limiting cyclization or related side reactions. The polymers **3** were of high purity, as determined by elemental analysis, displayed good solubilities in common organic solvents, and were stable toward oxygen and moisture.

Upon synthesis, the thermal stabilities of **3** were evaluated using thermogravimetric analysis (TGA). Despite the relatively large number of nitrogen atoms present in the main chains of these materials, they were found to be thermally stable and exhibited decomposition temperatures (T_d) that were dependent on their structures. For example, the T_d of **3a**, which features tertiary N-alkyl groups, was found to occur at 154 °C (Figure 2 b); in contrast, **3g** which features primary N-alkyl groups did not decompose until 278 °C. In this latter material, the first decomposition proceeded cleanly with a mass loss nearly equal to two units of molecular nitrogen (N_2) per repeat unit (ca. 7 %) as previously observed for analogous small molecules.[23] Likewise, the thermal decomposition of **3d**–**g** presumably afforded the respective polyguanidines, which appear to be stable to temperatures approaching 400 °C; additional studies of these materials is underway.

Next, efforts shifted toward examining the electronic and photophysical properties of **3**. In THF, their absorption maxima ranged between $\lambda_{max} = 379$ and 485 nm, depending on their structure. Polymers prepared from **2b** absorbed at shorter wavelengths compared to those prepared from **2a** or **2c**, presumably because of the conjugation disrupting effect of the biphenyl linkage. Interestingly, the λ_{max} of a relatively low MW **3a** ($\bar{M}_n = 5.0$ kDa, $\lambda_{max} = 450$ nm)[24] was hypsochromically shifted relative to a high molecular weight analogue ($\bar{M}_n = 29.4$ kDa, $\lambda_{max} = 485$ nm). Given that the repeat unit molecular weight is 823 Da, the former corresponds to approximately six repeat units and approximately 36 repeat units for the latter. Qualitatively, the larger λ_{max} value for the higher molecular weight polymer suggests that the effective conjugation length of these materials exceeds six repeat units. The polymers **3c** and **3g**, comprising fluorenyl units in their main chains, exhibited fluorescence at 546 nm in THF at 25 °C ($\Phi < 0.2\,\%$; Figure 2 c).

Finally, to explore the suitability of these materials for optoelectronic applications, we sought to determine their electrochemical and conductive properties. The polymer **3a** was found to exhibit multiple, irreversible oxidations ranging from $E_{pa} = +0.15$ V to $+0.72$ V (versus SCE) using cyclic voltammetry.[25] Prompted by this result, the polymer was spin coated onto a glass slide and tested for electrical conductivity using a multipoint probe station.[26] Whereas virgin films were found to be insulating ($\sigma < 10^{-10}$ S cm^{-1}), they were rendered conductive ($\sigma = 4 \times 10^{-3}$ S cm^{-1}) after exposure to iodine vapor for 24 hours. This value compares well with other classes of doped conjugated aromatic polymers, containing carbon–nitrogen double bonds, reported in the literature.[1a,7]

In conclusion, we have developed a novel, efficient, and practical route to a new class of polymers by using NHC/azide coupling chemistry. The combination of bis(NHC)s with complementary bis(azide)s produced a variety of thermally stable polytriazenes which exhibited good optical and electronic properties, as well as high solubilities in common organic solvents. To the best of our knowledge, this is the first example of using stable, free bis(NHC)s as polymer building blocks and effectively opens a new design strategy in synthetic polymer chemistry for accessing aromatic polymers containing carbon–nitrogen double bonds. Considering the large number of methods known for modifying the structures and electronic properties of NHCs[10] as well as organic azides,[27] the polymers reported herein are well-adapted for use in a variety of optoelectronic applications.

Received: February 23, 2009
Revised: May 5, 2009

Keywords: azides · carbenes · click chemistry · coupling reactions · polymers

---

[1] For early reports on these materials, see: a) C. S. Marvel, W. S. Hill, *J. Am. Chem. Soc.* **1950**, *72*, 4819–4820; b) B. G. Zimmerman, H. L. Lochte, *J. Am. Chem. Soc.* **1936**, *58*, 948–949; c) R. Adams, R. E. Bullock, W. C. Wilson, *J. Am. Chem. Soc.* **1923**, *45*, 521–527.

[2] For recent reviews, see: a) A. Iwan, D. Sek, *Prog. Polym. Sci.* **2008**, *33*, 289–345; b) M. Grigoras, C. O. Catanescu, *J. Macromol. Sci. Part C* **2004**, *44*, 131–173.

[3] a) S. Destri, M. Pasini, C. Pelizzi, W. Porzio, G. Predieri, C. Vignali, *Macromolecules* **1999**, *32*, 353–360; b) T. Matsumoto, F. Yamada, T. Kurosaki, *Macromolecules* **1997**, *30*, 3547–3552; c) C.-J. Yang, S. A. Jenekhe, *Macromolecules* **1995**, *28*, 1180–1196; d) C.-J. Yang, S. A. Jenekhe, *Chem. Mater.* **1991**, *3*, 878–887.

[4] a) P. W. Wojtkowski, *Macromolecules* **1987**, *20*, 740–748; b) P. W. Morgan, S. L. Kwolek, T. C. Pletcher, *Macromolecules* **1987**, *20*, 729–739.

[5] a) F.-C. Tsai, C.-C. Chang, C.-L. Liu, W.-C. Chen, S. A. Jenekhe, *Macromolecules* **2005**, *38*, 1958–1966; b) Y. Takihana, M. Shiotsuki, F. Sanda, T. Masuda, *Macromolecules* **2004**, *37*, 7578–7583; c) M. S. Weaver, D. D. C. Bradley, *Synth. Met.* **1996**, *83*, 61–66; d) W. Fischer, F. Stelzer, F. Meghdadi, G. Leising, *Synth. Met.* **1996**, *76*, 201–204; e) C.-J. Yang, S. A. Jenekhe, *Chem. Mater.* **1994**, *6*, 196–203.

[6] a) P. K. Dutta, P. Jain, P. Sen, R. Trivedi, P. K. Sen, J. Dutta, *Eur. Polym. J.* **2003**, *39*, 1007–1011; b) S. C. Suh, S. C. Shim, *Synth. Met.* **2000**, *114*, 91–95; c) J. McElvain, S. Tatsuura, F. Wudl, A. J. Heeger, *Synth. Met.* **1998**, *95*, 101–105; d) S. Di Bella, I. Fragala, I. Ledoux, M. A. Diaz-Garcia, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 9550–9557; e) S. A. Jenekhe, C.-J. Yang, H. Vanherzeele, J. S. Meth, *Chem. Mater.* **1991**, *3*, 985–987.

[7] a) İ. Kaya, S. Koyuncu, S. Çulhaoğlu, *Polymer* **2008**, *49*, 703–714; b) A. G. El-Shekeil, M. A. Khalid, F. A. Al-Yusufy, *Macromol. Chem. Phys.* **2001**, *202*, 2971–2979; c) S. C. Ng, H. S. O. Chan, P. M. L. Wong, K. L. Tan, B. T. G. Tan, *Polymer* **1998**, *39*, 4963–4968; d) S. Banerjee, P. K. Gutch, C. Saxena, *J. Polym. Sci. Part A* **1995**, *33*, 1719–1725.

[8] a) K. Yamamoto, M. Higuchi, S. Shlki, M. Tsuruta, H. Chiba, *Nature* **2002**, *415*, 509–511; b) M. Cano, L. Oriol, M. Pinol, J. L. Serrano, *Chem. Mater.* **1999**, *11*, 94–100; c) I. Manners, H. R. Allcock, G. Renner, O. Nuyken, *J. Am. Chem. Soc.* **1989**, *111*, 5478–5480.

[9] For selected examples, see: a) J. Miyake, Y. Chujo, *Macromolecules* **2008**, *41*, 9677–9682; b) J. Miyake, Y. Chujo, *Macromolecules* **2008**, *41*, 5671–5673; c) D. Nepal, S. Samal, K. E. Geckeler, *Macromolecules* **2003**, *36*, 3800–3802; d) T. Matsumoto, T. Matsuoka, Y. Suzuki, K. Miyazawa, T. Kurosaki, T. Mizukami, *Macromol. Symp.* **2003**, *199*, 83–96; e) O. Thomas, O. Inganaes, M. R. Andersson, *Macromolecules* **1998**, *31*, 2676–2678; f) T. E. Olinga, S. Destri, C. Botta, W. Porzio, R. Consonni, *Macromolecules* **1998**, *31*, 1070–1078; g) R. Gauderon, J. G. C. Plummer, J. G. Hilborn, *Macromolecules* **1998**, *31*, 501–507; h) P. Cerrada, L. Oriol, M. Pinol, J. L. Serrano, I. Iribarren, Munoz S. Guerra, *Macromolecules* **1996**, *29*, 2515–2523; i) S. B. Park, H. Kim, W. C. Zin, J. C. Jung, *Macromolecules* **1993**, *26*, 1627–1632.

[10] For reviews on NHCs, see: a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; b) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921; c) W. A. Herrmann, K. Kocher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.

[11] a) D. M. Khramov, C. W. Bielawski, *J. Org. Chem.* **2007**, *72*, 9407–9417; b) D. M. Khramov, C. W. Bielawski, *Chem. Commun.* **2005**, 4958–4960.

[12] a) E. Kleinpeter, B. A. Stamboliyska, *J. Org. Chem.* **2008**, *73*, 8250–8255; b) J. Preat, C. Michaux, A. Lewalle, E. A. Perpete, D. Jacquemin, *Chem. Phys. Lett.* **2008**, *451*, 37–42.

[13] D. J. Coady, C. W. Bielawski, *Macromolecules* **2006**, *39*, 8895–8897.

[14] For other classes of triazo containing polymers, see: a) B. Erb, J. P. Kucma, S. Mourey, F. Struber, *Chem. Eur. J.* **2003**, *9*, 2582–2588; b) O. Nuyken, U. Dahn, *J. Polym. Sci. Part A* **1997**, *35*, 3017–3025; c) O. Nuyken, U. Dahn, W. Ehrfeld, V. Hessel, K. Hesch, J. Landsiedel, J. Diebel, *Chem. Mater.* **1997**, *9*, 485–494; d) O. Nuyken, C. Scherer, A. Baindl, A. R. Brenner, U. Dahn, R. Gärtner, S. Kaiser-Röhrich, R. Kollefrath, P. Matusche, B. Voit, *Prog. Polym. Sci.* **1997**, *22*, 93–183.

[15] a) C. W. Tomøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; b) H. C. Kolb, M. G. Finn, B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[16] a) J.-F. Lutz, *Angew. Chem.* **2007**, *119*, 1036–1043; *Angew. Chem. Int. Ed.* **2007**, *46*, 1018–1025; b) D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen, J. N. H. Reek, *Chem. Commun.* **2005**, 4333–4335; c) P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. I. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless, V. V. Fokin, *Angew. Chem.* **2004**, *116*, 4018–4022; *Angew. Chem. Int. Ed.* **2004**, *43*, 3928–3932; d) B. Helms, J. L. Mynar, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2004**, *126*, 15020–15021.

[17] a) D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332–6335; *Angew. Chem. Int. Ed.* **2006**, *45*, 6186–6189; b) A. J. Boydston, C. W. Bielawski, *Dalton Trans.* **2006**, 4073–4077; c) A. J. Boydston, K. A. Williams, C. W. Bielawski, *J. Am. Chem. Soc.* **2005**, *127*, 12496–12497.

[18] Bis(NHC)s featuring less sophisticated N-substituents (e.g., ethyl, *n*-butyl, *tert*-butyl, etc.) are either prone to polymerization via NHC dimerization (see: J. W. Kamplain, C. W. Bielawski, *Chem. Commun.* **2006**, 1727–1729) or produced insoluble materials upon combination with **2**. As a result, such bis(NHC)s were not extensively examined.

[19] U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477–487.

[20] This calculation assumes no cyclic polymer formation and a statistical polymerization reaction where the polymers produced have an average of one azide end group and one NHC end group per chain.

[21] Polytriazenes **3** were found to undergo protonation in the presence of moderate to strong acids. In their protonated forms, they did not readily elute from the GPC columns employed and necessitated the use of a basic elution mixture (THF/pyridine 9:1).

[22] Polymers obtained from the combination of **1b** and **2a** as well as **1b** and **2b** were found to be insoluble in common organic solvents. The T_d values of these materials were found to be 273 °C.

[23] This result was consistent with previous studies showing that the decomposition products of triazenes derived from NHCs with 1° alkyl substituents are molecular nitrogen and its respective guanidine; see reference [11a].

[24] This polymer was prepared from **1a** and **2a** using a 10% molar excess of the latter monomer.

[25] $E_{pa} = +0.15$, $+0.40$, and $+0.72$ V. Conditions: CH_2Cl_2 as the solvent, 0.1 M $[n\text{Bu}_4\text{N}][\text{PF}_6]$ as the electrolyte, 1 mM **3a**, scan rate = 0.1 $V\,s^{-1}$, referenced to Fc/Fc^+ (Fc = ferrocene; $E_{1/2} =$ 0.45 V versus a saturated calomel electrode, SCE).

[26] Polymers were spin coated from CH_2Cl_2 onto glass slides containing gold electrodes spaced at 1 mm, 2 mm, and 5 mm intervals. Film thickness was measured using a surface profiler and were found to be approximately 1 μm. Conductivity measurements of the polymer films were measured by a two-point probe linear sweep voltammetry.

[27] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320–5374; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240.