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Synthesis of Polybenzoquinolines as Precursors for Nitrogen-Doped Graphene Nanoribbons**

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Abstract: *Graphene nanoribbons (GNRs) represent promising materials for the next generation of nanoscale electronics. However, despite substantial progress towards the bottom-up synthesis of chemically and structurally well-defined all-carbon GNRs, strategies for the preparation of their nitrogen-doped analogs remain at a nascent stage. This scarce literature precedent is surprising given the established use of substitutional doping for tuning the properties of electronic materials. Herein, we report the synthesis of a previously unknown class of polybenzoquinoline-based materials, which have potential as GNR precursors. Our scalable and facile approach employs few synthetic steps, inexpensive commercial starting materials, and straightforward reaction conditions. Moreover, due to the importance of quinoline derivatives for a variety of applications, the reported findings may hold implications across a diverse range of chemical and physical disciplines.*

Graphene nanoribbons (GNRs), which are narrow strips of graphene featuring a quantum confinement-induced bandgap, constitute a promising class of materials for the next generation of semiconductor devices.[1–10] The electronic properties of GNRs are exquisitely sensitive to their width, heteroatom content, and edge character.[3–5] Thus, much research effort has been devoted to the preparation of GNRs that are structurally and chemically defined at the atomic level.[6–10] Although traditional top-down lithographic approaches have exhibited only limited success in this regard,[6–10] more recent studies have demonstrated the bottom-up preparation of pristine GNRs via the surface-assisted[11–22] or solution-phase[23–32] synthesis of nanoribbon precursor polymers, followed by their cyclodehydrogenation. To date, these bottom-up strategies have primarily focused on all-carbon systems, with only a limited number of studies describing the preparation of nitrogen-containing GNR frameworks.[20–22,31,32] Given the immense potential of substitutional nitrogen doping for tailoring the properties of GNRs, the sparse literature precedent is surprising and likely arises from the challenges associated with the incorporation of heteroatoms at arbitrary locations in graphitic materials.[33,34]

Herein, we describe the modular synthesis of polybenzoquinolines, which constitute a generic class of GNR precursor polymers, and, to the best of our knowledge, have never been previously reported. We first develop general aza-Diels–Alder reaction conditions for the synthesis of a series of benzoquinoline model compounds. Subsequently, we prepare an AB-type bifunctional monomer and use the conditions validated for the model compounds to synthesize a congested polybenzoquinoline via a Diels–Alder-type polymerization reaction.[35–37] We in turn demonstrate the scope and modularity of our methodology by preparing polybenzoquinolines of various sizes that feature different peripheral substituents. Overall, our findings enable facile and rapid access to a previously unknown family of benzoquinoline-based materials, which may prove valuable for a wide range of applications.

As our synthetic target, we selected a nitrogen-doped $N=7$ armchair GNR (Figure 1, left). We envisioned the preparation of this target by surface-assisted cyclodehydrogenation of a polymeric precursor, as demonstrated by Müllen, Fasel, and co-workers for the conversion of polyanthracenes into analogous unsubstituted, all-carbon, GNRs.[11–13] Here, to enable the formation of a well-defined nitrogen-doped GNR, we designed an alternative unreported precursor consisting of benzoquinoline subunits linked at their 4 and 6 positions (Figure 1, middle). We in turn drew inspiration from the synthesis of quinoline heterocycles via the aza-Diels–Alder (Povarov) reaction[38–44] and pictured the construction of the benzoquinoline subunits from alkyne- and aldimine-modified monomers (Figure 1, right). Consequently, we postulated that polymerization of the bifunctional monomers would furnish the desired polybenzoquinoline precursor (Figure 1, middle), which could ultimately be cyclodehydrogenated into a nitrogen-doped $N=7$ armchair GNR (Figure 1, left).

We began our studies by synthesizing benzoquinoline model compounds **3a,b** and **5a,b** via the Povarov reaction,[38–44] as illustrated in Scheme 1a. To prepare model compounds **3a** and **3b**, we first formed aldimines **1a** and **1b** by using a known literature protocol.[45] We then reacted naphthyl alkyne **2** with **1a** or **1b** in the presence of $BF_3{\cdot}OEt_2$ as the Lewis acid mediator and chloranil as the sacrificial oxidant,[46–50] producing benzoquinolines **3a** or **3b**, respectively. Next, to prepare model compounds **5a** and **5b**, we

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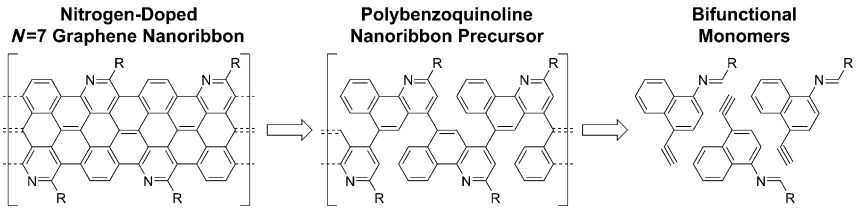
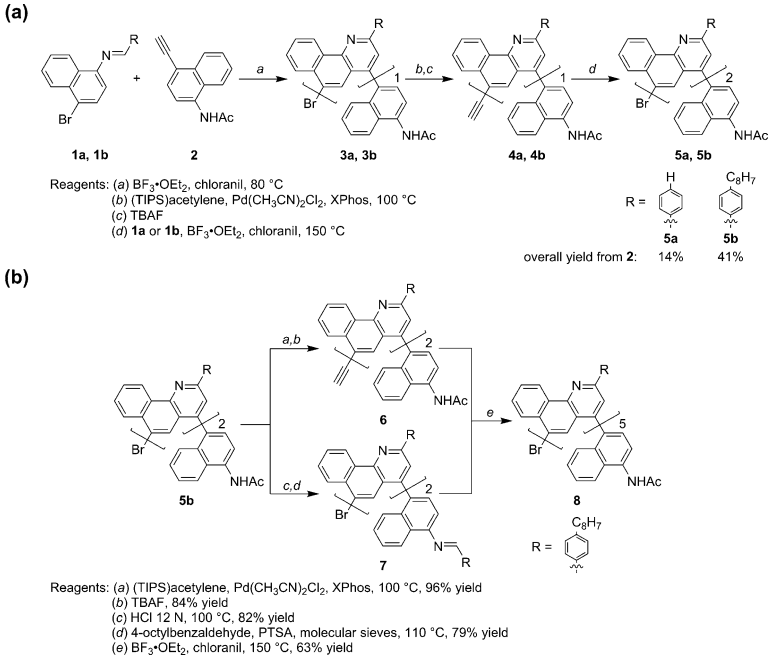


Figure 1. Illustration of a synthetic strategy for the preparation of a nitrogen-doped $N=7$ armchair graphene nanoribbon. The desired steps consist of the Diels–Alder-type polymerization of bifunctional monomers to furnish a polybenzoquinoline nanoribbon precursor, which can in turn be cyclodehydrogenated into the target nitrogen-doped graphene nanoribbon.



Scheme 1. a) Synthesis of benzoquinoline model compounds **3a**, **3b**, **5a**, and **5b** (TIPS = triisopropylsilyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, TBAF = tetrabutylammonium fluoride). b) Synthesis of benzoquinoline model compound **8** (PTSA = *p*-toluenesulfonic acid).

converted the pendant bromides of compounds **3a** and **3b** to alkynes, forming **4a** and **4b**, respectively. We then reacted alkyne **4a** with aldimine **1a**, producing benzoquinolines **5a,** and alkyne **4b** with aldimine **1b**, producing benzoquinoline **5b**. This linear synthetic strategy furnished the desired regioisomerically pure products in moderate yields.

We in turn sought to prepare pentameric compound **8** as a longer model benzoquinoline (Scheme 1b). To construct **8**, we used **5b** as the sole starting material and generated complementary building blocks **6** and **7**. Thus, to synthesize **6**, we converted the pendant bromide of **5b** to an alkyne, and to synthesize **7**, we converted the acetyl-protected amine of **5b** to an aldimine. We subsequently combined alkyne **6** and aldimine **7** under our standard Povarov conditions, furnishing compound **8**. Here, by independently modifying the bromide and amine termini of our precursors, we avoided an arduous linear synthesis to produce a benzoquinoline macromolecule.

We characterized our benzoquinoline model compounds (**3a**, **3b**, **5a**, **5b**, and **8**) with ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and/or X-ray crystallography (see the Supporting Information for details). In particular, we grew crystals of **3a** and **5a** and determined their solid-state structures through standard X-ray crystallography techniques (Figure 2).[51] Although the resolution of **5a** was poor, both crystal structures confirmed that our reaction conditions produced only the desired regioisomers and connectivity, as further supported by a detailed NMR analysis for **3b** (Figures S1–S9). The crystal structures also revealed that the naphthyl moieties of both **3a** and **5a** were almost completely orthogonal with respect to their neighboring benzoquinoline subunits (Figure 2a,b) and that the two constituent benzoquinoline subunits of **5a** were twisted out of planarity with respect to one another (Figure 2b). Altogether, these experiments definitively confirmed the identity of our compounds.

With our model compounds in hand, we proceeded to prepare an elongated benzoquinoline macromolecule. Thus, we produced polybenzoquinoline **11a** through polymerization of an AB-type bifunctional monomer via the Povarov reaction. To this end, we first synthesized monomer **10a** from 4-iodonaphthylamine **9** in only three steps (Scheme 2a). The design of **10a** incorporated the requisite alkyne and aldimine functional groups within a single substrate, as well as an alkyl chain for enhanced solubility. We next used the reaction conditions optimized for the synthesis of **3b**, **5b**, and **8** (Scheme 1) to polymerize **10a**, furnishing polybenzoquinoline **11a** (Scheme 2a). We analyzed the resulting reaction mixture via size-exclusion chromatography with a refractive index detector (SEC-RI), and through calibration with standards, we obtained a number average molecular weight (M_n) of 2730 g mol^{-1}, a weight average molecular weight (M_w) of 5420 g mol^{-1}, and a polydispersity index (PDI) of 1.98 for crude **11a** (See the Supporting Information for details and Figure S10.). The PDI of the crude product was consistent with a step-growth polymerization mechanism, as expected for a Diels–Alder-type reaction.[35–37]

We subsequently processed and again characterized polybenzoquinoline **11a**. We first terminated the reaction by addition of phenylacetylene and purified the resulting material through sequential precipitation/chromatography (see the Supporting Information for details). We then analyzed **11a** by SEC-RI with respect to calibration standards. Our measurement yielded a M_n of 7840 g mol^{-1}, a M_w of 10500 g mol^{-1}, and a PDI of 1.34, corresponding to about 21 main chain benzoquinoline subunits for purified **11a** (Figure 3 and Table 1). For comparison, the same measurement for monodisperse benzoquinoline model compound **8** yielded a M_n of 2110 g mol^{-1}, a M_w of 2120 g mol^{-1}, and a PDI of 1.01,

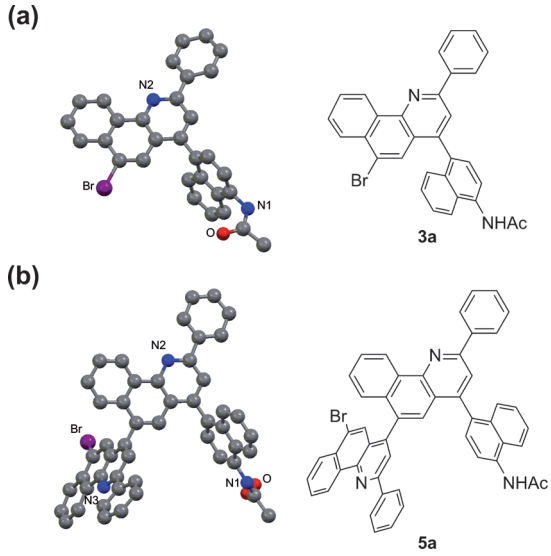
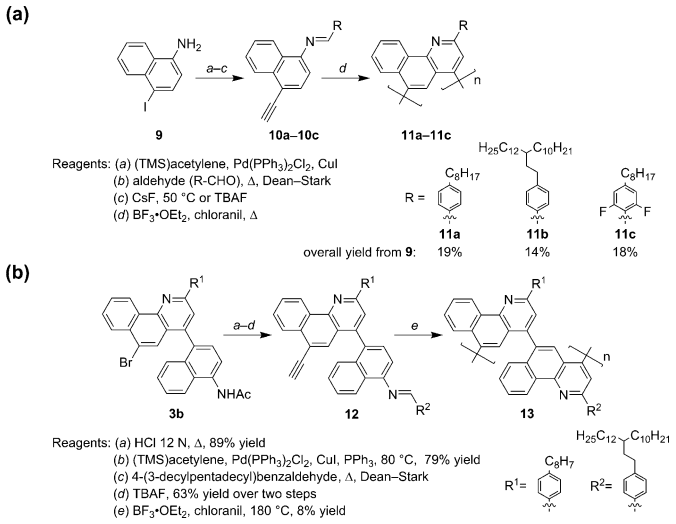


Figure 2. a) The X-ray crystal structure and the corresponding chemical structure for benzoquinoline **3a**. b) The X-ray crystal structure and the corresponding chemical structure for benzoquinoline **5a**. For both crystal structures, the carbon, nitrogen, oxygen, and bromine atoms are indicated in gray, blue, red, and purple, respectively. Note that the hydrogen atoms and solvent molecules have been omitted for clarity.

confirming the accuracy of our analysis (Figure 3 and Table 1). Notably, despite its aromatic character and crowded architecture, **11a** was readily soluble in most common organic solvents, presumably due to a partially contorted geometry, as observed for our model compounds in the solid state. Our observations were consistent with the preparation of an extended polybenzoquinoline.

We further characterized **3b**, **5b**, **8**, and **11a** with ultraviolet-visible (UV/Vis) spectroscopy (Figure 4). The spectra obtained for **3b**, **5b**, and **8** showed characteristic absorbance peaks with maxima at nearly identical positions of 297, 314,



Scheme 2. a) Synthesis of monomers **10a–10c** and polybenzoquinolines **11a–11c** (TMS = trimethylsilyl). b) Synthesis of monomer **12** and polybenzoquinoline **13**.

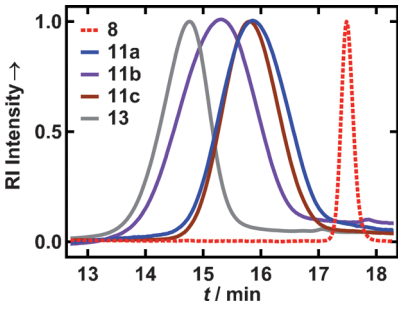


Figure 3. The SEC-RI chromatograms obtained for polybenzoquinolines **11a** (solid blue line), **11b** (solid purple line), **11c** (solid brown line), and **13** (solid gray line), as well as for benzoquinoline model compound **8** (dashed red line). The chromatograms have been normalized for clarity.

Table 1: The tabulated M_n, M_w, and PDI values for **8**, **11a**, **11b**, **11c**, and **13**, as calculated from the chromatograms in Figure 3. Note the excellent agreement between the calculated and actual molecular weights of **8**.

Compound	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI	n[b]
8	2110[a]	2120[a]	1.01	5
11a	7840	10500	1.34	21
11b	15500	22300	1.44	25
11c	8960	10900	1.22	22
13	29600	36200	1.22	60

[a] The actual molecular weight is 2093 g mol^{-1}. [b] The approximate number of benzoquinoline subunits, as estimated from M_n.

352, and 370 nm. By comparison, the spectrum obtained for **11a** featured broadened absorption maxima at similar positions and an onset of absorption that was red-shifted from 380 to 450 nm. Together, these measurements corroborated the formation of an extended polybenzoquinoline system for **11a**.

We next sought to demonstrate that our polymerization strategy was modular and capable of accommodating different peripheral substituents. Thus, we leveraged the reaction conditions already validated for the synthesis of **10a** to prepare monomers **10b** and **10c**, which incorporated branched alkyl chain and fluorine substituents, respectively (Scheme 2a). We then used conditions similar to those developed for the synthesis of **3b**, **5b**, **8**, and **11a** to furnish polybenzoquinoline **11b** from **10b** and polybenzoquinoline **11c** from **10c** (Scheme 2a). Our standard purification and analysis procedures yielded the data shown in Figure 3 and Table 1 for **11b** and **11c**, confirming the success of our polymerization reactions. The preparation of distinct polybenzoquinolines under similar conditions underscored the potential general scope of our approach.

Finally, we applied our polymerization strategy to the preparation of an even longer, sequence-variable polybenzoquinoline macromolecule. We slightly modified the procedure required for the preparation of **10a–10c** to convert **3b** into bifunctional monomer **12** in four steps (Scheme 2b). The design of **12** incorporated the requisite alkyne and aldimine functional groups, an expanded aromatic core containing an

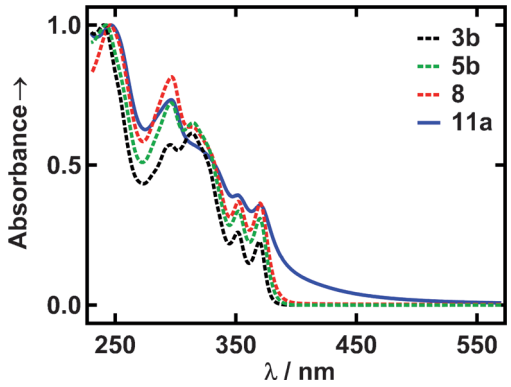


Figure 4. The UV/Vis absorbance spectra obtained for benzoquinoline model compounds **3b** (dashed black line), **5b** (dashed green line), and **8** (dashed red line), as well as polybenzoquinoline **11a** (solid blue line). Note that the spectrum of the polybenzoquinoline is broadened and red-shifted with respect to the spectra of the model compounds. The spectra have been normalized for clarity.

additional benzoquinoline subunit, and alternating linear and branched alkyl side chains. Polymerization of **12** under our standard reaction conditions furnished polybenzoquinoline **13**. Per our SEC-RI measurement, this polymer featured a M_n of 29600 g mol^{-1}, a M_w of 36200 g mol^{-1}, and a PDI of 1.22, corresponding to about 60 main chain benzoquinoline subunits (Figure 3 and Table 1). Moreover, despite its increased size relative to **11a**–**11c**, **13** exhibited good solubility in common organic solvents. Overall, these findings demonstrated the potential modularity of our approach, portending favorably for the synthesis of polybenzoquinoline-based graphene nanoribbon precursors with tunable sequence contexts.

In summary, we have developed a new methodology for the preparation of polybenzoquinolines, which is significant for several reasons. First, the aza-Diels–Alder (Povarov) reaction has been employed for the synthesis of benzoquinolines only in a limited number of previous instances.[40–44] To the best of our knowledge, the current study represents the first reported synthesis of modular polybenzoquinolines using the Povarov (or any other) reaction. Second, our scalable approach employs few synthetic steps, inexpensive precursor materials, and straighforward reaction conditions. These advantageous features facilitate the preparation of crowded yet soluble polymers with variable peripheral substituents and sizes. Given the large number of commercially available benzaldehyde derivatives, our strategy may also provide access to a diverse family of benzoquinoline-based materials. Third, the reported polybenzoquinolines constitute a novel class of precursor polymers for $N=7$ armchair GNRs (Figure 1), which have been prepared exclusively from polyanthracenes to date.[11–19] Due to the propensity of some anthracene derivatives to oxidation and undesirable photochemistry,[52,53] our precursors may prove advantageous for the preparation of diverse libraries of GNRs with designer electronic properties. Finally, we note that our polybenzoquinolines could find a number of alternative applications; indeed, quinoline derivatives are privileged scaffolds in medicinal chemistry,[54,55] ubiquitous ligands in inorganic chemistry,[56,57] and promising materials for organic electronic devices.[58–61] Consequently, the presented synthetic methodology may prove generally valuable across a broad swath of chemical and physical disciplines.

Keywords: graphene nanoribbons · nanotechnology · organic electronics · polymers · quinolines

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[1] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183–191.
[2] F. Schwierz, *Nat. Nanotechnol.* **2010**, *5*, 487–496.
[3] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, *81*, 109–162.
[4] S. Dutta, S. K. Pati, *J. Mater. Chem.* **2010**, *20*, 8207–8223.
[5] O. V. Yazyev, *Acc. Chem. Res.* **2013**, *46*, 2319–2328.
[6] L. Chen, Y. Hernandez, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2012**, *51*, 7640–7654; *Angew. Chem.* **2012**, *124*, 7758–7773.
[7] Z. Chen, Y.-M. Lin, M. J. Rooks, P. Avouris, *Physica E* **2007**, *40*, 228–232.
[8] L. Ma, J. Wang, F. Ding, *ChemPhysChem* **2013**, *14*, 47–54.
[9] M. Terrones, A. R. Botello-Méndez, J. Campos-Delgado, F. López-Urías, Y. I. Vega-Cantú, F. J. Rodríguez-Macías, A. L. Elías, E. Muñoz-Sandoval, A. G. Cano-Márquez, J.-C. Charlier, H. Terrones, *Nano Today* **2010**, *5*, 351–372.
[10] K. Müllen, *ACS Nano* **2014**, *8*, 6531–6541.
[11] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, *Nature* **2010**, *466*, 470–473.
[12] P. Ruffieux, J. Cai, N. C. Plumb, L. Patthey, D. Prezzi, A. Ferretti, E. Molinari, X. Feng, K. Müllen, C. A. Pignedoli, R. Fasel, *ACS Nano* **2012**, *6*, 6930–6935.
[13] S. Blankenburg, J. Cai, P. Ruffieux, R. Jaafar, D. Passerone, X. Feng, K. Müllen, R. Fasel, C. A. Pignedoli, *ACS Nano* **2012**, *6*, 2020–2025.
[14] L. Talirz, H. Söde, J. Cai, P. Ruffieux, S. Blankenburg, R. Jafaar, R. Berger, X. Feng, K. Müllen, D. Passerone, R. Fasel, C. A. Pignedoli, *J. Am. Chem. Soc.* **2013**, *135*, 2060–2063.
[15] R. Denk, M. Hohage, P. Zeppenfeld, J. Cai, C. A. Pignedoli, H. Söde, R. Fasel, X. Feng, K. Müllen, S. Wang, D. Prezzi, A. Ferretti, A. Ruini, E. Molinari, P. Ruffieux, *Nat. Commun.* **2014**, *5*, 4253.
[16] M. Koch, F. Ample, C. Joachim, L. Grill, *Nat. Nanotechnol.* **2012**, *7*, 713–717.
[17] C. Bronner, M. Utecht, A. Haase, P. Saalfrank, T. Klamroth, P. Tegeder, *J. Chem. Phys.* **2014**, *140*, 024701.
[18] H. Sakaguchi, Y. Kawagoe, Y. Hirano, T. Iruka, M. Yano, T. Nakae, *Adv. Mater.* **2014**, *26*, 4134–4138.
[19] A. Batra, D. Cvetko, G. Kladnik, O. Adak, C. Cardoso, A. Ferretti, D. Prezzi, E. Molinari, A. Morgante, L. Venkataraman, *Chem. Sci.* **2014**, *5*, 4419–4423.
[20] C. Bronner, S. Stremlau, M. Gille, F. Brauße, A. Haase, S. Hecht, P. Tegeder, *Angew. Chem. Int. Ed.* **2013**, *52*, 4422–4425; *Angew. Chem.* **2013**, *125*, 4518–4521.
[21] J. Cai, C. A. Pignedoli, L. Talirz, P. Ruffieux, H. Söde, L. Liang, V. Meunier, R. Berger, R. Li, X. Feng, K. Müllen, R. Fasel, *Nat. Nanotechnol.* **2014**, *9*, 896–900.
[22] Y. Zhang, Y. Zhang, G. Li, J. Lu, X. Lin, S. Du, R. Berger, X. Feng, K. Müllen, H.-J. Gao, *Appl. Phys. Lett.* **2014**, *105*, 023101.
[23] X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Räder, K. Müllen, *J. Am. Chem. Soc.* **2008**, *130*, 4216–4217.
[24] L. Dössel, L. Gherghel, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2011**, *50*, 2540–2543; *Angew. Chem.* **2011**, *123*, 2588–2591.

[25] M. G. Schwab, A. Narita, Y. Hernandez, T. Balandina, K. S. Mali, S. De Feyter, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2012**, *134*, 18169 – 18172.
[26] Y.-Z. Tan, B. Yang, K. Parvez, A. Narita, S. Osella, D. Beljonne, X. Feng, K. Müllen, *Nat. Commun.* **2013**, *4*, 2646.
[27] K. T. Kim, J. W. Jung, W. H. Jo, *Carbon* **2013**, *63*, 202 – 209.
[28] A. Narita, X. Feng, Y. Hernandez, S. A. Jensen, M. Bonn, H. Yang, I. A. Verzhbitskiy, C. Casiraghi, M. R. Hansen, A. H. R. Koch, G. Fytas, O. Ivasenko, B. Li, K. S. Mali, T. Balandina, S. Mahesh, S. De Feyter, K. Müllen, *Nat. Chem.* **2014**, *6*, 126 – 132.
[29] A. Narita, I. A. Verzhbitskiy, W. Frederickx, K. S. Mali, S. A. Jensen, M. R. Hansen, M. Bonn, S. De Feyter, C. Casiraghi, X. Feng, K. Müllen, *ACS Nano* **2014**, *8*, 11622 – 11630.
[30] T. H. Vo, M. Shekhirev, D. A. Kunkel, M. D. Morton, E. Berglund, L. Kong, P. M. Wilson, P. A. Dowben, A. Enders, A. Sinitskii, *Nat. Commun.* **2014**, *5*, 3189.
[31] K. T. Kim, J. W. Lee, W. H. Jo, *Macromol. Chem. Phys.* **2013**, *214*, 2768 – 2773.
[32] T. H. Vo, M. Shekhirev, D. A. Kunkel, F. Orange, M. J.-F. Guinel, A. Enders, A. Sinitskii, *Chem. Commun.* **2014**, *50*, 4172 – 4174.
[33] R. Lv, M. Terrones, *Mater. Lett.* **2012**, *78*, 209 – 218.
[34] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, *2*, 781 – 794.
[35] W. J. Bailey in *Step-Growth Polymerizations* (Ed.: D. H. Solomon), Marcel Dekker, New York, **1972**, pp. 279 – 332.
[36] A. D. Schlüter in *Synthesis of Polymers* (Ed.: A.-D. Schlüter), Wiley-VCH, Weinheim, **2008**, pp. 459 – 483.
[37] M. A. Tasdelen, *Polym. Chem.* **2011**, *2*, 2133 – 2145.
[38] L. S. Povarov, *Russ. Chem. Rev.* **1967**, *36*, 656 – 670.
[39] V. V. Kouznetsov, *Tetrahedron* **2009**, *65*, 2721 – 2750.
[40] Y. Zhang, P. Li, L. Wang, *J. Heterocycl. Chem.* **2011**, *48*, 153 – 157.
[41] C. Yao, B. Qin, H. Zhang, J. Lu, D. Wang, S. Tu, *RSC Adv.* **2012**, *2*, 3759 – 3764.
[42] R. Suresh, S. Muthusubramanian, R. Senthilkumaran, G. Manickam, *J. Org. Chem.* **2012**, *77*, 1468 – 1476.
[43] M. M. Sarmah, D. Bhuyan, D. Prajapati, *Synlett* **2013**, *24*, 2245 – 2248.
[44] G. Maiti, R. Karmakar, U. Kayal, *Tetrahedron Lett.* **2013**, *54*, 2920 – 2923.
[45] K. Taguchi, F. H. Westheimer, *J. Org. Chem.* **1971**, *36*, 1570 – 1572.
[46] E. A. Braude, J. Hannah, R. Linstead, *J. Chem. Soc.* **1960**, 3249 – 3257.
[47] R. Huisgen, M. Seidel, G. Wallbillich, H. Knupfer, *Tetrahedron* **1962**, *17*, 3 – 29.
[48] R. I. Fryer, J. V. Earley, E. Evans, J. Schneider, L. H. Sternbach, *J. Org. Chem.* **1970**, *35*, 2455 – 2459.
[49] B. E. Landberg, J. W. Lown, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1326 – 1333.
[50] D. R. Buckle, Chloranil, *e-EROS Encyclopedia of Reagents for Organic Synthesis*, Wiley Hoboken, **2001**, http://onlinelibrary.wiley.com/doi/10.1002/047084289X.rc057/pdf.
[51] CCDC 1051858 (**3a**) and CCDC 1051857 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
[52] J. C. C. Atherton, S. Jones, *Tetrahedron* **2003**, *59*, 9039 – 9057.
[53] A. R. Reddy, M. Bendikov, *Chem. Commun.* **2006**, 1179 – 1181.
[54] S. Kumar, S. Bawa, H. Gupta, *Mini-Rev. Med. Chem.* **2009**, *9*, 1648 – 1654.
[55] V. R. Solomon, H. Lee, *Curr. Med. Chem.* **2011**, *18*, 1488 – 1508.
[56] A. Kimyonok, X.-Y. Wang, M. Weck, *J. Macromol. Sci. Polym. Rev.* **2006**, *46*, 47 – 77.
[57] V. Prachayasittikul, S. Prachayasittikul, S. Ruchirawat, V. Prachayasittikul, *Drug Des. Dev. Ther.* **2013**, *7*, 1157 – 1178.
[58] S. A. Jenekhe, X. Zhang, X. L. Chen, V.-E. Choong, Y. Gao, B. R. Hsieh, *Chem. Mater.* **1997**, *9*, 409 – 412.
[59] M. S. Liu, Y. Liu, R. C. Urian, H. Ma, A. K.-Y. Jen, *J. Mater. Chem.* **1999**, *9*, 2201 – 2204.
[60] X. Zhang, A. S. Shetty, S. A. Jenekhe, *Macromolecules* **1999**, *32*, 7422 – 7429.
[61] C. J. Tonzola, M. M. Alam, S. A. Jenekhe, *Macromolecules* **2005**, *38*, 9539 – 9547.

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