Aryne Polymerization Enabling Straightforward Synthesis of Elusive Poly(*ortho*-arylene)s

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Ⓢ *Supporting Information*

ABSTRACT: Herein we present the first straightforward aryne polymerization that successively connects aromatic rings at their *ortho*-positions, *directly* giving poly(*ortho*-phenylene)s of up to ca. 100-mer size. The polymerization proceeds smoothly in a chain-growth fashion in the presence of a monovalent copper reagent. Direct synthesis of poly(*ortho*-arylene)s has been a "missing piece" of aromatic chemistry for a long time (although the discovery of arynes dates back to 1902), in contrast to the well-investigated *para*- and *meta*-linked polyarylenes. Our achievement reported here is expected to open up new areas of nanocarbon and materials science.

W ell-regulated linkage of aromatic rings is a central issue in fundamental synthetic chemistry and materials science.[1] An aryne, formed by abstraction of two hydrogen atoms from an aromatic compound, is one of the oldest-known aromatic reactive intermediates[2] and has a distorted triple bond within the ring, resulting in a low-lying LUMO that is associated with extremely high reactivity and a short lifetime. Aryne chemistry has been extensively studied both experimentally and theoretically since its discovery over 100 years ago and plays key roles in many fields, including reaction development, total synthesis of natural products, and functionalization of nanomaterials.[3] However, the polymerization of arynes has remained elusive. In 2005, Ihara et al. reported that all their attempts to polymerize an aryne using a wide range of initiators (Grignard reagent, transition metals, radical species, etc.) under various conditions were unsuccessful.[4] In 2014, Ito and Nozaki et al. developed a *formal* aryne polymerization through polymerization of [2.2.1]oxabicyclic alkenes followed by dehydration of the resultant polymers.[5] They noted that they adopted this approach because polymerization of an aryne is extremely challenging due to its uncontrollable, high reactivity. Now, we report the first polymerization of an aryne that enables *direct* synthesis of poly(*ortho*-arylene)s, consisting of aromatic units successively connected through the *ortho*-position.

For *in situ* aryne generation, we selected a well-established protocol, i.e., the combination of an *o*-trimethylsilyl triflate precursor and fluorine anion (Scheme 1).[6] After extensive experimentation to screen initiators, including various organic/organometallic reagents, we found that the use of a Lipshutz-

**Scheme 1. Polymerization of Arynes[8] (Solvent = THF or Acetonitrile)**
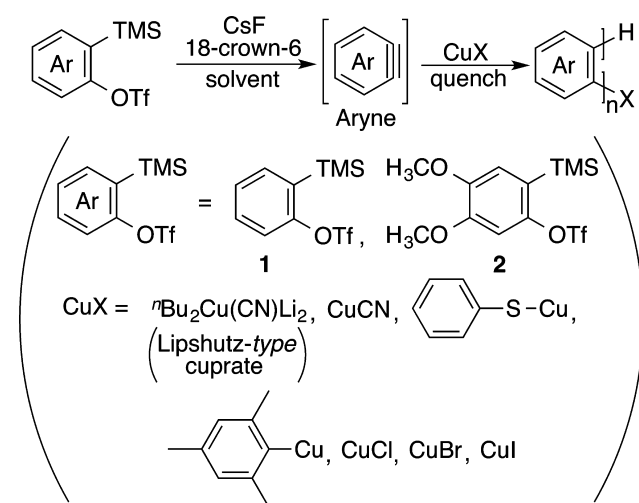
type cuprate,[7] a copper ate complex prepared from 1 equiv of CuCN and 2 equiv of *n*BuLi, for the polymerization of **1** in THF gave an insoluble white solid. The attenuated total reflection (ATR) infrared spectrum of the solid showed absorptions attributable to C−H bond and C≡C double bond stretching vibrations of the aromatic moiety at around 3000 and 1500 cm^{-1}, respectively (Figure S1). This strongly suggested that the insoluble solid was not an inorganic salt, but an organic compound. The insolubility prevented further analysis, but we speculated that the solid might be poly-(*ortho*-phenylene).

Installing dimethoxy side chains on the benzene ring of the precursor allowed us to access additional information about the structure of the product. When 4,5-dimethoxyl 2-(trimethyl-silyl)phenyl triflate **2** was used as a precursor, we obtained a yellow material that was soluble in various common organic solvents. Consumption of **2** was complete within 6 h, as monitored by gas chromatography (GC) coupled with mass spectrometry. Gel permeation chromatography (GPC) indicated that the material included polymeric compounds. The crude product was purified by means of recycling preparative

high-performance liquid chromatography (HPLC), affording a polymer in 32% yield (M_n = 2380, M_w = 3250 and PDI = 1.36). These values indicated that ca. 18 monomer units were present in the polymer molecule. As shown in Figure 1a, the proton
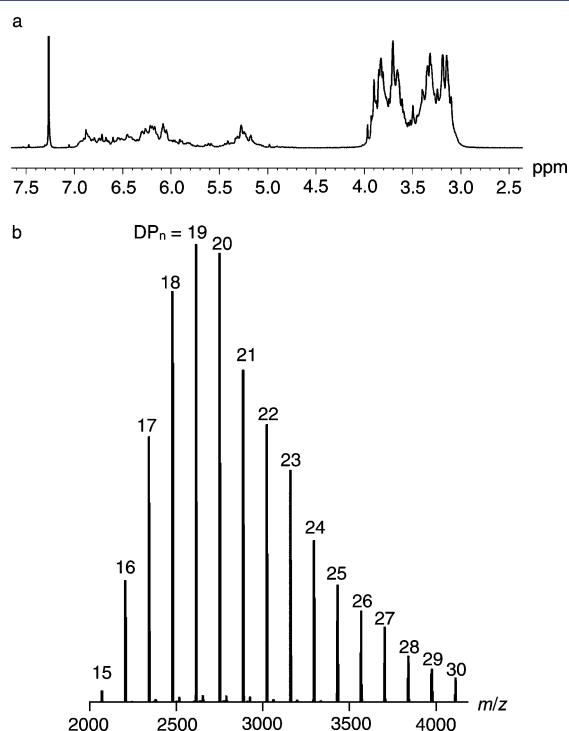

Figure 1. (a) ^{1}H NMR spectrum in CDCl$_3$ and (b) MALDI-TOF mass spectrum of poly(*ortho*-phenylene) (M_n = 2380, M_w = 3250 and PDI = 1.36) obtained by polymerization of **2** with Lipshutz-type cuprate in THF. DP$_n$ is the degree of polymerization.

nuclear magnetic resonance (^{1}H NMR) spectrum in deuterated chloroform (CDCl$_3$) exhibited aromatic proton signals in the range from 4.78 to 7.01 ppm and dimethoxy group proton signals at 2.78−4.13 ppm, which are in good agreement with those of oligo(*ortho*-phenylene)s synthesized in a stepwise manner by Fukushima and Aida et al.[9,10] This strongly supported the view that polymerization of an aryne had proceeded to afford a poly(*ortho*-phenylene). Furthermore, similar signals of long oligomeric products were observed in acetonitrile-d_3 (Figure S2),[9] providing further support for the formation of *ortho*-linkages in the polymerization.

Well-regulated polymer growth was confirmed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry of the obtained polymer (Figure 1b). Detailed analysis of the spectrum revealed that the mass-to-charge ratio (m/z) values could be expressed as 136.05 × n + 1.0 (H) + 26.0 (CN), where n is equal to the number of repeating units, indicating that a single cyano group existed in each polymer chain, and the polymer structure was NC-(*ortho*-phenylene)$_n$-H. The expected peak for the 19-mer would be at m/z 136.05 × 19 (repeating unit) + 1.0 (H) + 26.0 (CN) = 2612.0, and a peak was observed at m/z 2612.2. We had initially supposed that the ^{n}Bu ligand on the cuprate would initiate the polymerization, leading to the 19-mer with ^{n}Bu/H ends, which should show a peak at m/z 2643.1, but no such peak was observed.

The employment of CuCN as the initiator in place of the cuprate resulted in effective and smooth polymerization at

room temperature to give the poly(*ortho*-phenylene) (Figure 2). Furthermore, a broad range of monovalent copper salts,
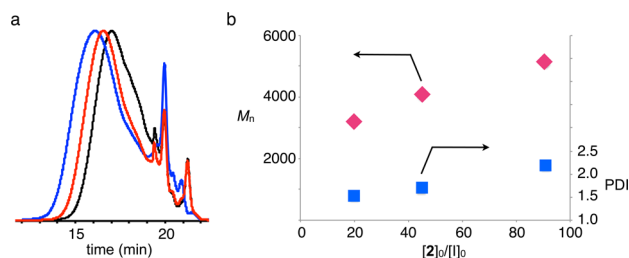
Figure 2. (a) GPC profile of the crude products obtained by polymerization of **2** with CuCN as an initiator in THF using CsF/18-crown-6 ether at various feed ratios; [**2**]$_0$/[I] = 20 (black line), 45 (red line), and 91 (blue line). (b) Plots of M_n (magenta diamond) and PDI (blue square) versus [**2**]$_0$/[I].

such as thiophenolate, mesitylate, chloride, bromide, and iodide, also promoted the polymerization to afford the desired poly(*ortho*-phenylene)s (Table S1, Figures S3 and S6−S11).[8] It is noteworthy that the use of mesityl copper as an initiator in acetonitrile gave ca. 100-mer polymer (M_n = 13 830 g/mol, M_w = 20 840 g/mol, PDI = 1.50) (Figure S4). A polymerization reaction did not occur or scarcely proceeded with CuBr$_2$, KCN, Zn(CN)$_2$, AuCl, AuClSMe$_2$, or Pd$_2$(dba)$_3$ as the initiator, or without any initiator (Figure S5). The polymerization with CuCN proceeded even in the presence of 9,10-dihydroxy-anthracene as a radical scavenger and took place in the dark, indicating that the polymerization is not initiated/promoted by a radical species or by light. Thus, monovalent copper salts appear to play a crucial role in the aryne polymerization.

As shown in Table 1 and Figure 2, the value of M_n of the obtained polymers could be regulated by adjusting the feed

Table 1. Polymerization of 2 with CuCN as an Initiator in THF Using CsF/18-Crown-6 at Various Feed Ratios

entry	[**2**]$_0$/[I]$_0$	$M_n{}^a$	$M_w{}^a$	PDI^a
1	20	3220	4970	1.54
2	45	4050	6890	1.70
3	91	5100	11 160	2.19

^{a}These values were determined by GPC, calibrated with polystyrene standards.

ratio of **2** and initiator ([**2**]$_0$/[I]$_0$). In other words, varying the initiator amount enabled us to modulate the molecular weight of the resultant poly(*ortho*-arylene)s. This result supports the idea that the polymerization proceeds in a chain-growth fashion, not through step growth.

We next performed density functional theory (DFT) calculations to understand the polymerization mechanism.[11] Global reaction route mapping (GRRM) analysis[12] indicated that the reaction pathway of polymerization of benzyne initiated by CuCN (Figure 3) is the most probable. According to this pathway, the present aryne polymerization proceeds through a coordination/insertion mechanism. The complex-ation of CuCN to benzyne occurs first to provide a triangular complex (**CP1**), which serves as the precursor for the polymerization. The stabilization energy is very large (29.6 kcal/mol) because of an energetically and geometrically favorable interaction between the high-lying d-orbital of copper(I) and the low-lying LUMO of the aryne, and this
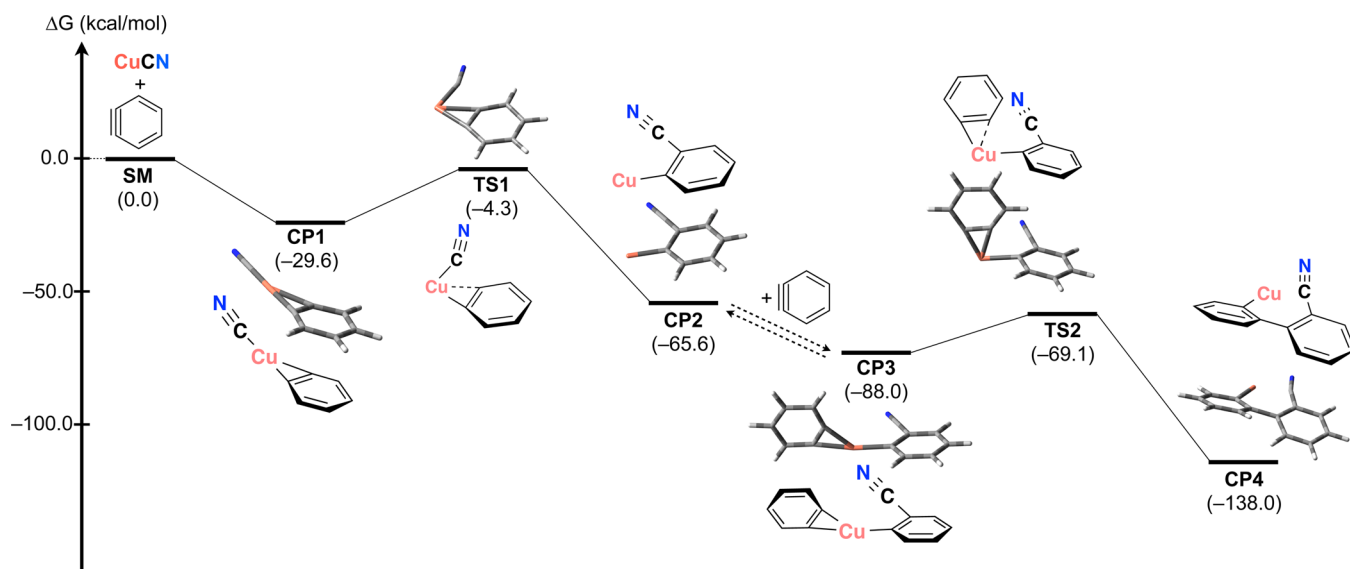
Figure 3. A plausible reaction pathway of the polymerization. Energy diagram of the coordination/insertion reaction pathway based on density functional theory calculation at the B3LYP/6-31+G(d)-LANL2DZ(Cu) level.

appears to be the reason why a wide range of Cu(I) reagents can promote this unique polymerization. Through **TS1**, the benzyne triple bond inserts into the Cu−CN bond to form **CP2** with an activation energy of 25.3 kcal/mol and a large energy gain (−61.3 kcal/mol). Intermediate **CP2** then forms a π-complex **CP3** with the second benzyne, and insertion of the benzyne proceeds with an activation barrier of 18.9 kcal/mol to give a biphenyl copper(I) intermediate **CP4** with high exothermicity.

Unique properties and the potential utility of various oligo-/poly(*ortho*-arylene)s have recently been *partially* demonstrated through *indirect* approaches.[9,13,14] Ito and Suginome et al. developed a synthesis of poly(quinoxaline-2,3-diyl)s through an aromatization approach with a palladium catalyst and reported that the products showed helical geometry with potential application in dynamic chiral catalysts and in solid polymer films to selectively reflect circularly polarized light.[13] Fukushima and Aida et al. reported an iterative stepwise approach to access poly(*ortho*-phenylene)s, which showed a redox-responsive spring motion based on an accumulated π-cloud along the helical axis and acted as surface modifiers for homeotropic columnar ordering of discotic liquid crystals.[9,14b,c] However, the lack of simple and straightforward synthetic methodology for *ortho*-substituted aromatic materials has hindered the development of innovative materials, in marked contrast to the ready accessibility of *para*- and *meta*-substituted materials,[15] and a direct polymerization method for poly(*ortho*-arylene)s has long been regarded as a "missing piece" of aromatic chemistry.[14a,b,15a,16] We believe the *direct* approach, the aryne polymerization reported here, will provide robust access to a range of so-far-unexplored or poorly accessible poly(*ortho*-arylene) materials.

In conclusion, after more than 100 years of aryne chemistry, we present the first aryne polymerization, providing straightforward methodology for the direct synthesis of elusive poly-(*ortho*-arylene)s, which have a range of potential applications in nanocarbon chemistry and materials science.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental and theoretical section; GPC, ^{1}H NMR, ^{13}C NMR, IR, and MALDI-TOF MS data; and discussion of the polymerization mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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