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BBr$_3$-promoted cyclization to produce ladder-type conjugated polymer

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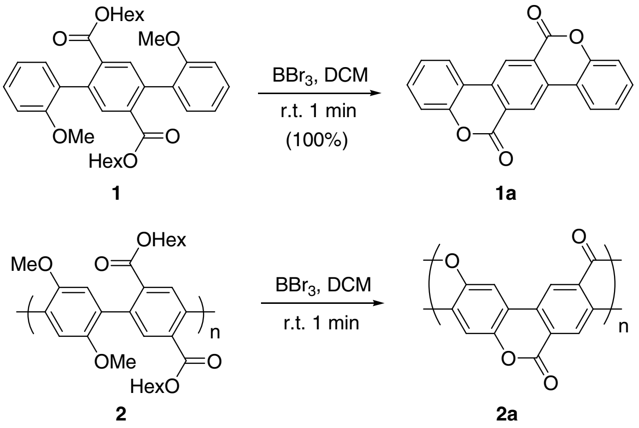
Abstract—A novel chemical cyclization method using BBr$_3$ has been successfully developed to prepare ladder-type conjugated systems. The cyclized ladder compounds revealed an extended conjugation due to planarization of the structures. The extended ladder polymer can also be easily prepared by our chemical cyclization method using a soluble precursor.

The synthesis of organic semiconductors has been extensively developed in recent years due to the opportunity to fabricate low-cost and/or large-area electronic components.[1] While new materials are being introduced,[2] ladder-type and planar π-conjugated molecular architectures are current topics in material chemistry because the rigid and planar framework of ladder molecules is expected to improve the properties for application, including the degree of π-conjugation and environmental stability.[3]

These rigid systems are, however, generally insoluble because of their strong π-stacking interactions, which limit their purification to vacuum sublimation methods. Owing to the major impact of impurity on the performance of organic electronic devices, the definition of synthetic methods allowing simple and straightforward purification of organic semiconductors appears as a key issue for the development of new materials. Several groups have reported the preparation of soluble, thermally or photochemically sensitive, precursors allowing the direct formation of active films of ladder-type compounds based on mainly pentacene derivatives.[4] Nevertheless, the synthetic route is not generally applicable to longer conjugated systems because of the extremely poor solubility of the longer polymers.

We report herein novel chemical cyclization methods designed to efficiently produce ladder-type conjugated systems including extended ones.

Chemical cyclization of compound **1** was promoted by the addition of BBr$_3$ in dichloromethane (DCM) solution. Phenoxide, generated by BBr$_3$-promoted demethylation, acted as a nucleophile for acyl substitution with the neighboring ester group, thus causing it to lactonize (Scheme 1).[5] This method constitutes a significant improvement over other precursor routes to produce ladder-type conjugated systems because the reaction is



Scheme 1. Synthesis of the ladder-type compounds **1a** and its extended polymeric structure **2a** using BBr$_3$-promoted lactonization.

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fast and quantitative. Furthermore, any by-products formed are easily removed as the cyclized compound **1a** is sparingly soluble in most solvents. This procedure also avoids the use of organometallic catalyst for C–C coupling reactions in the last step of the synthesis, whose presence, even as traces, may alter the electronic properties of the organic semiconductors.

Single crystals, grown by slow evaporation of a solution of **1a** in chloroform, have been analyzed by X-ray diffraction.[6,7] The crystal structure, selected bond lengths and angles for **1a** are presented in Figure 1. The molecular structure of compound **1a** confirms the expected planar structure and the X-ray crystal packing structure reveals that it is arranged by cofacial π-stacking motifs (Fig. 1). Well-ordered structure along the a axis is also observed in crystal packing.

The electronic properties of **1a** were studied by UV–vis and fluorescence spectroscopies and compared to the corresponding non-cyclized precursor **1**. As expected, the λ_{max} of **1a** is red-shifted compared to that of **1** in both absorption and emission, which indicates that the cyclization leads to an extended conjugation.[8]

The extended ladder molecule **2a** was obtained from polymer **2** using BBr_3 in dichloromethane by the same procedure as described above (Scheme 1). The IR spectrum showed that a strong carbonyl signal due to a lactone at 1731 cm^{-1} was predominant for **2a**, compared with that of an ester (1720 cm^{-1}) for **2**, and this was consistent with the results from the model compounds **1** and **1a** (1721 $cm^{-1}$for **1** and 1732 cm^{-1} for **1a**). Based on the model studies (Scheme 1), we estimate that the conversion to the cyclized polymer **2a** was complete, however, further studies are required for full structure determination and/or purity assessment of **2a**.

Synthesis of the precursor **2** for the extended ladder-type polymer **2a** was achieved by employing the Pd-catalyzed cross-coupling protocol using the corresponding diboronic acid **3** and dibromo ester **4** (Scheme 2).[9] Polymer **2** shows a good solubility in dichloromethane and can thus be easily purified by Soxhlet method. The cyclized polymer **2a** was not soluble in most solvents, and stable against air and moisture because of its rigid structure.

Cyclization of the polymer **2** was successfully achieved not only in solution but also on films. Figure 2 shows

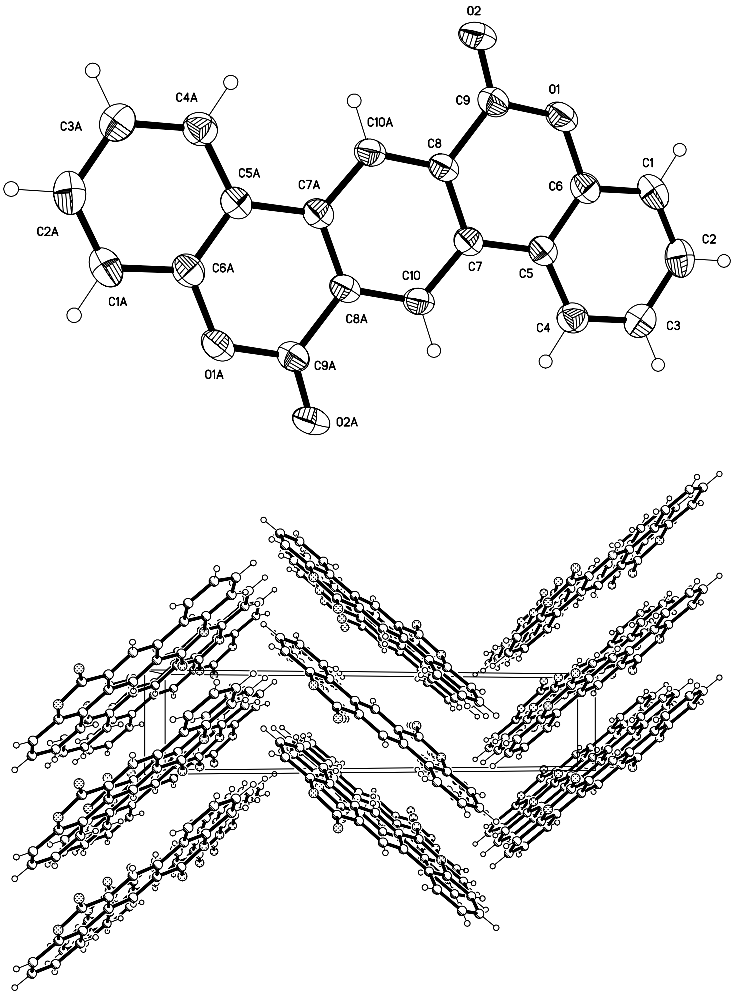
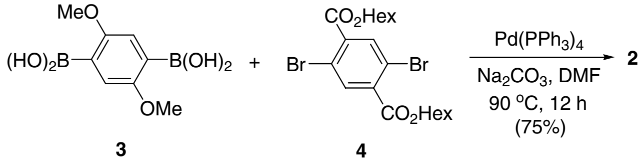


Figure 1. Molecular Structure of **1a** along the atom numbering scheme (top) and the packing diagram viewing down the a axis (bottom). Selected bond lengths (Å) and bond angles (°); C6-O1:1.3882(17), C9-O1:1.3638(18), C8-C9-O1:117.66(13), C9-O1-C6:122.52(11).



Scheme 2. Synthesis of the precursor polymer **2** using Pd-catalyzed cross-coupling reaction.

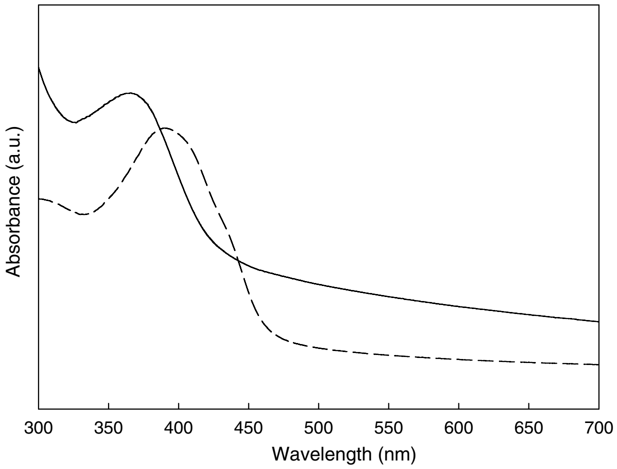
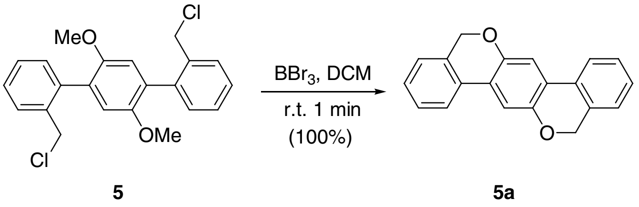


Figure 2. UV–vis spectra of precursor polymer **2** (solid line) and its cyclized form **2a** (dotted line) on films. The spectrum of **2a** was obtained after dipping the film of **2** into a solution of BBr_3 (1.0 M in hexane) and a little amount of dichloromethane for 1 min, followed by washing with methanol and water. See Supplementary data for details.

the UV–vis absorption spectra of compounds **2** and **2a** on films. The spectrum of compound **2** shows an absorption maximum at 366 nm. In contrast, compound **2a** shows a maximum at 390 nm, which confirms that the planarization of the structure due to the cyclization makes an effective extended conjugation.

The possibility to prepare thin-films of the ladder-type conjugated polymer associated with the electronic properties of **2a** and its planar conformation incites us to realize field-effect transistors using **2a** as an active semiconductor layer. We expect that this novel cyclized conjugated polymer with a planar structure would provide high mobility, together with significant environmental stability. Possibilities of the prepared films for organic field effect transistors are currently under investigation.

Finally, to further exploit our chemical cyclization route using BBr_3, we have also attempted to produce the ether-type ladder molecule **5a**. Phenoxide, generated by BBr_3-promoted demethylation in **5**,[10] caused nucleophilic substitution with the benzyl chloride to the desired cyclized benzyl ether **5a** in a quantitative yield (Scheme 3).



Scheme 3. BBr_3-promoted cyclization to produce the ladder-type aromatic ether **5a**.

The cyclized ether **5a**, having an electron-donor, was regarded as a suitable model for constructing a p-type polymer, whereas the cylized ester with an electron-acceptor **1a** would be a n-type counterpart. An extended ether polymer with ladder-type structure is under synthesis.

In summary, we have successfully developed novel chemical methods to produce ladder-type conjugated systems using soluble precursors. The conjugated precursor can be easily purified, and straightforward and quantitative cyclization led to the planarization of the extended π-conjugated systems.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.020.

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5. As a few examples, BBr_3-promoted cyclization was used to prepare 5- or 6-membered ring in the synthesis of Vernolepin and Vernomenin. Grieco, P. A.; Nishizawa, M.; Oguri, T.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* **1977**, *99*, 5773.
6. *X-ray crystallographic analysis*: The crystal of **1a** was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, operating at 50 kV and 30 mA, and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 298 K. The data collection 2θ ranges for **1a** is 4.00–57.00. The first 50 frames were retaken after complete data collection and compared. The crystal showed no significant decay and no corrections were applied for the decay. The raw data were processed to give structure factors using the SAINT program.[11] The structure was solved by direction methods and refined by full matrix least squares against F^2 for all data using SHELXTL software (version 5.10).[12] All non-hydrogen atoms in compound **1a** were anisotropically refined. All hydrogen atoms were placed in idealized positions and refined using a riding model. The crystal system in compound **1a** belongs to the monoclinic and $P2_1/c$ space group. Crystallographic data in CIF format for the structure reported here have been deposited at the Cambridge Crystallographic Data Centre (Deposition No. CCDC-617985). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].
7. The crystal data, together with the refined atomic coordinates and anisotropic thermal parameters, for **1a** and experimental procedures for the syntheses of all compounds are available in the Supplementary data.
8. For **1**, $\lambda_{max} = 315$ nm; $\varepsilon = 4780\ M^{-1}\,cm^{-1}$; emission $\lambda_{max} = 425$ nm and **1a**, $\lambda_{max} = 328$ nm; $\varepsilon = 70{,}000\ M^{-1}\,cm^{-1}$; emission $\lambda_{max} = 433$ nm in dichloromethane. It should be also mentioned that a large Stokes shift was observed for **1a** despite its rigid planar structure, and there are no rational explanations on this at the current state.
9. The GPC analysis of the polymer **2** revealed molecular weights of $M_n = 7.1 \times 10^3$ and $M_w = 1.2 \times 10^4$, respectively.
10. Synthesis of the compound **5** requires the conversion of the corresponding benzyl alcohol to the benzyl chloride as direct cross-coupling reaction using benzyl chloride gave the product in low yield (10%). See Supplementary data for details.
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