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Division of Materials Chemistry – Polymer Controlled Synthesis –

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Scope of Research

Our research focuses on creation of new organic molecules with potential as key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. For example, we are developing a new living radical polymerization method using heavier heteroatom compounds as controlling agents. Another topic is the synthesis of cycloparaphenylenes, hoop-shaped π -conjugated molecules, based on new synthetic strategies. We also study various condensed states of polymers by both static and dynamic methods to understand the relationship between structure and physical properties.

KEYWORDS

Organic Synthesis Polymer Synthesis Living Radical Polymerization
Polymer Properties Curved π -Conjugated Molecules



Selected Publications

Fan, W.; Nakamura, Y.; Yamago, S., Synthesis of Multivalent Organotellurium Chain Transfer Agents by Post-modification and Their Applications in Living Radical Polymerization, *Chem. Eur. J.*, **22**, 17006-17010 (2016).
Nakamura, Y.; Lee, R.; Coote, M.; Yamago, S., Termination Mechanism of the Radical Polymerization of Acrylates: Elucidation of the Reactivity of Polymer-end and Mid-chain Radicals, *Macromol. Rapid Commun.*, **37**, 506-513 (2016).
Kayahara, E.; Patel, V. K.; Mercier, A.; Kündig, E. P.; Yamago, S., Regioselective Synthesis and Characterization of Multinuclear Convex-bounded Ruthenium-[n]Cycloparaphenylene (n = 5 and 6) Complexes, *Angew. Chem. Int. Ed.*, **55**, 302-306 (2016).
Kayahara, E.; Fukayama, K.; Nishinaga, T.; Yamago, S., Size Dependence of [N]Cycloparaphenylenes (N = 5-12) in Electrochemical Oxidation, *Chem. Asian J.*, **11**, 1793-1797 (2016).
Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S., Synthesis and Characterization of [n]CPP (n = 5, 6, 8, 10, and 12) Radical Cation and Dications: Size-Dependent Absorption, Spin, and Charge Delocalization, *J. Am. Chem. Soc.*, **138**, 338-344 (2016).

Practical Synthesis of [n]Cycloparaphenylenes ($n = 5, 7-12$) by H_2SnCl_4 -mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors

Cyclic precursors of cycloparaphenylenes (CPPs) containing 1,4-dihydroxy-2,5-cyclohexadien-1,4-diyl units were prepared by modifying the synthesis method of corresponding 1,4-dimethoxy derivatives, which was developed by Jasti and co-workers. Reductive aromatization of the diyl moieties by $\text{SnCl}_2/2\text{HCl}$ took place under mild conditions and afforded CPPs incorporating 5 or 7–12 phenylene units with good yield. Highly strained [5]CPP was synthesized at more than 0.3 g. ^{119}Sn NMR spectroscopy clarified the *in situ* formation of an ate complex, H_2SnCl_4 , upon mixing a 2:1 ratio of HCl and SnCl_2 , which serves as a highly active reducing agent under nearly neutral conditions. When more than two equivalents of HCl, in relation to SnCl_2 , were used, acid-catalyzed decomposition of the CPP precursors took place. The stoichiometry of HCl and SnCl_2 was found to be critical in achieving the desired aromatization reaction of highly strained CPP precursors.

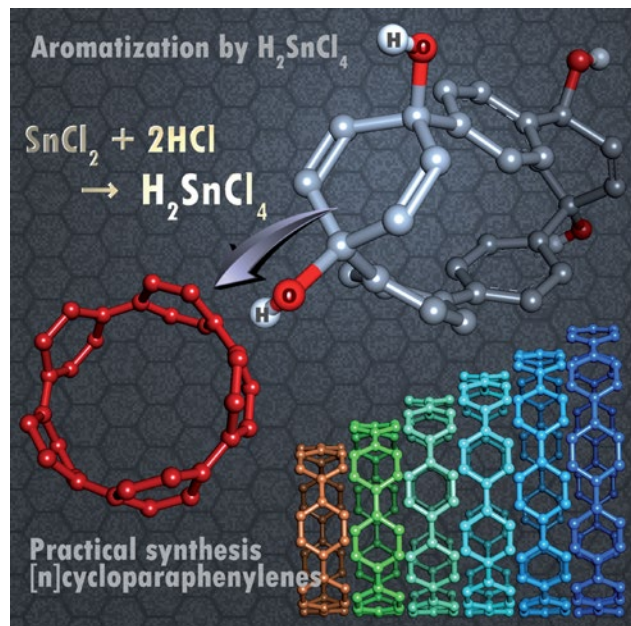


Figure 1. Synthesis of [n]Cycloparaphenylenes ($n = 5, 7-12$).

Synthesis of Multivalent Organotellurium Chain-Transfer Agents by Post-modification and Their Applications in Living Radical Polymerization

Multivalent or functionalized organotellurium chain-transfer agents (CTAs) for living radical polymerization were synthesized by post-modification. The synthesis involving the condensation between a carboxylic-acid-functionalized CTA and various amines proceeded in excellent yields without affecting the reactive tellurium moiety. The CTAs exhibited high synthetic versatility for radical polymerization and gave structurally well-controlled polymers, such as multiarmed polymers, from various monomers. Because all new CTAs are easily available on a large scale by simple purification, the current method significantly facilitates macromolecular engineering based on organotellurium-mediated radical polymerization (TERP).

