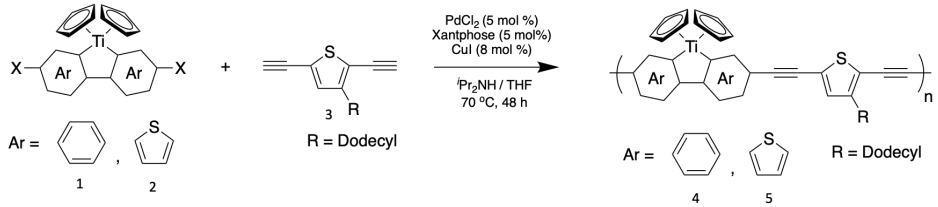
Synthesis of π-Conjugated Organometallic Polymers Containing Fused Titanacycle and Thiophene Units

([1]*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Alvin Tanudjaja,[1] Ryoyu Hifumi,[1] Shinsuke Inagi,[1] and Ikuyoshi Tomita[1]
Keywords: π-conjugated polymers, fused ring, titanacycle, thiophene

π-Conjugated polymers possessing heteroles of transition metals would be potentially attractive materials for optoelectronic applications on the basis of the d-electrons of the transition metals. We have been working on the synthesis of titanacyclopentadiene-containing polymers by the reaction of aromatic diynes and a low-valent titanium complex, which serve as useful synthetic precursors for π-conjugated polymers containing heteroatoms.[1] Based on the advantages of fused heterole systems, we have also reported the synthesis of π-conjugated polymers containing titanafluorene[2] and dithienotitanacyclopentadiene moieties.[3] Herein we describe the synthesis of polymers containing both thiophene and fused titanacycles so as to obtain polymers with advanced optoelectronic performances.

As monomers for the polycondensation processes, a 4,4'-dibromotitanafluorene derivative (**1**) was prepared by the lithiation of 4,4'-dibromo-2,2'-diiodobiphenyl using *n*-BuLi followed by the reaction with titanocene dichloride, while 5,5'-diido-bithiophene (**2**) was prepared by the reaction of dithienotitanacyclopentadiene with *N*-iodosuccinimide. The arylene dihalides possessing titanacycle moieties thus obtained (**1** and **2**) were subjected to the Sonogashira-Hagihara polycondensation using 3-dodecyl-2,5-diethynylthiophene (**3**) in the presence of a palladium catalyst to produce the corresponding polymers (**4** and **5**). Unique optical and electronic properties of the resulting polymers will also be described.



1) a) K. Atami, T. Kino, W. M. Zhou, H. Nishiyama, I. Tomita, *Synth. Met*. **2009**, *159*, 949; b) H. Nishiyama, I. Tomita, *Macromol. Chem. Phys*. **2010**, *20*, 2248; c) Y. Matsumura, M. Ueda, K. Fukuda, K. Fukui, I. Takase, H. Nishiyama, S. Inagi, I. Tomita, *ACS Macro Lett.* **2015**, *4*, 124; d) Y. Matsumura, K. Fukuda, S. Inagi, I. Tomita, *Macromol. Rapid Commun*. **2015**, *36*, 660; e) Y. Matsumura, M. Ishidoshiro, Y. Irie, H. Imoto, K. Naka, K. Tanaka, S. Inagi, I. Tomita, *Angew. Chem. Int. Ed*. **2016**, *55*, 15040;
2) A. Tanudjaja, S. Inagi, F. Kitamura, T. Takata, I. Tomita, *Dalton Trans*. **2021**, *50*, 3037-3043.
3) A. Tanudjaja, R. Hifumi, S. Inagi, I. Tomita, *Polymer* **2022**, *241*, 124511.