The Effect of the Secondary Ligand in the Nickel-mediated Dehalogenative Polycondensation of Dibromofluorene

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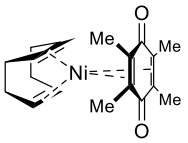
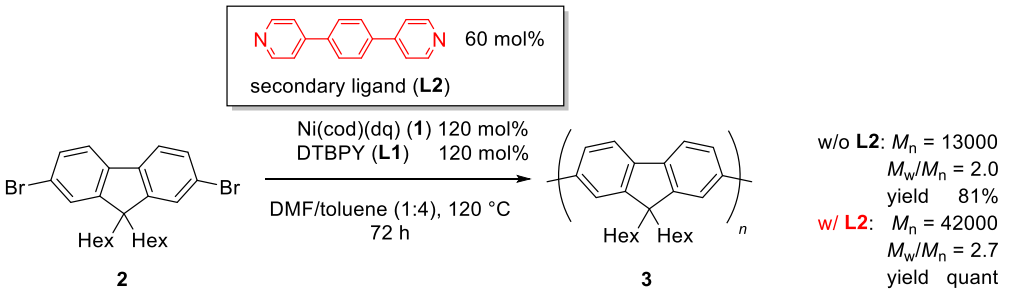
We have reported the dehalogenative polyfluorene synthesis using Ni(cod)(dq) (**1**) (COD: 1,5-cyclooctadiene, DQ: duroquinone) as a nickel(0) complex and DTBPY (**L1**) (4,4'-di-*tert*-butyl-2,2'-bipyridine) as a bipyridine ligand.[1] Herein, we describe the effect of the secondary ligand on the dehalogenative polycondensation.



Ni(cod)(dq) (**1**)

In our previous report, the polymerization of dibromofluorene **2** with Ni(cod)(dq) (**1**) and **L1** resulted in affording polyfluorene **3** (M_n = 13000) in 81% yield.[1] When 60 mol% 4,4'-bipyridine was employed as a secondary ligand, the molecular weight of **3** was decreased to M_n = 5100. However, the molecular wight of **3** was remarkably improved to M_n = 42000 with 1,4-bis(4-pyridyl)benzene (**L2**) (60 mol%) as a secondary ligand. In contrast, the polymerization hardly proceeded with 60 mol% of **L2** in the absence of bipyridine ligand **L1**.



2 **3**

Reference

1. Noda, N.; Umeda, M.; Okano, K.; Horie, M.; Mori, A. *ChemRxiv* **2024**, DOI: 10.26434/chemrxiv-2024-1rfzp.