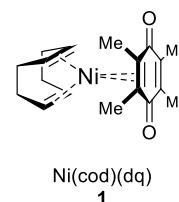


# The Use of Air-stable Nickel(0) Complex Ni(cod)(dq) for the Synthesis of $\pi$ -Conjugated Polymers by Dehalogenative Coupling Polycondensation

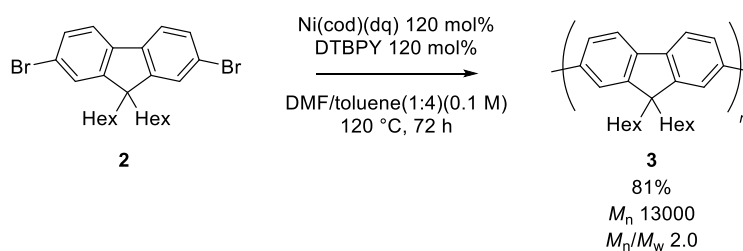
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**Keywords:** Ni(cod)(dq); bipyridine ligand; polyfluorene;  $\pi$ -conjugated polymer; dehalogenative polycondensation

Ni(cod)(dq) (**1**) (COD: 1,5-cyclooctadiene; DQ: duroquinone)<sup>1</sup> with an appropriate bipyridine ligand is shown to serve as an air-stable Ni<sup>0</sup> complex. We herein describe that nickel complex **1** is available for the dehalogenative polycondensation of dihaloarenes to afford  $\pi$ -conjugated polymers.<sup>2</sup>



The reaction of 2,7-dibromo-9,9-di(*n*-hexylfluorene) (**2**) with nickel complex composed of Ni(cod)(dq) and DTBPY (4,4'-di-*tert*-butyl-2,2'-bipyridine) in DMF/toluene (1:4) proceeded at 120 °C for 72 h. Polyfluorene **3** was obtained in 81% yield with  $M_n = 13000$  ( $M_w/M_n = 2.0$ ). It is remarkable that the use of Ni(cod)(dq) after the storage of the freshly opened one for several months afforded the corresponding polymer in a comparable yield and molecular weight. The dehalogenative polymerization with other dihaloarenes such as fluorene with different alkyl chain structures, 1,4- and 1,3-dihalobenzenes, 5,5'-dibromo-2,2'-bithiophene, and 2,6-dibromo-cyclopentadithiophene also proceeded to afford the corresponding conjugated polymers in excellent yields with an appropriate degree of polymerization.



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