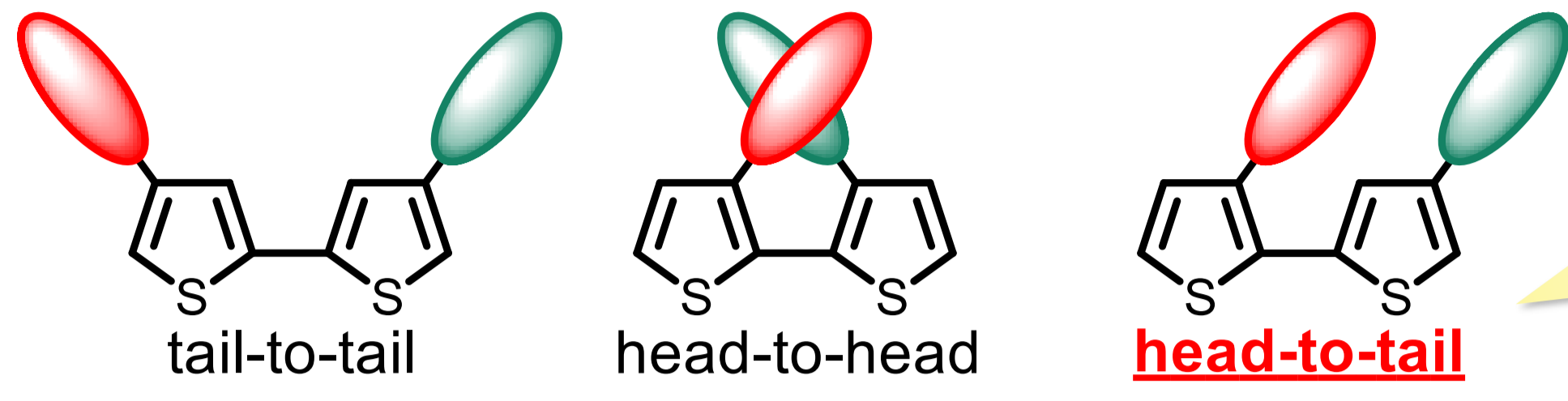
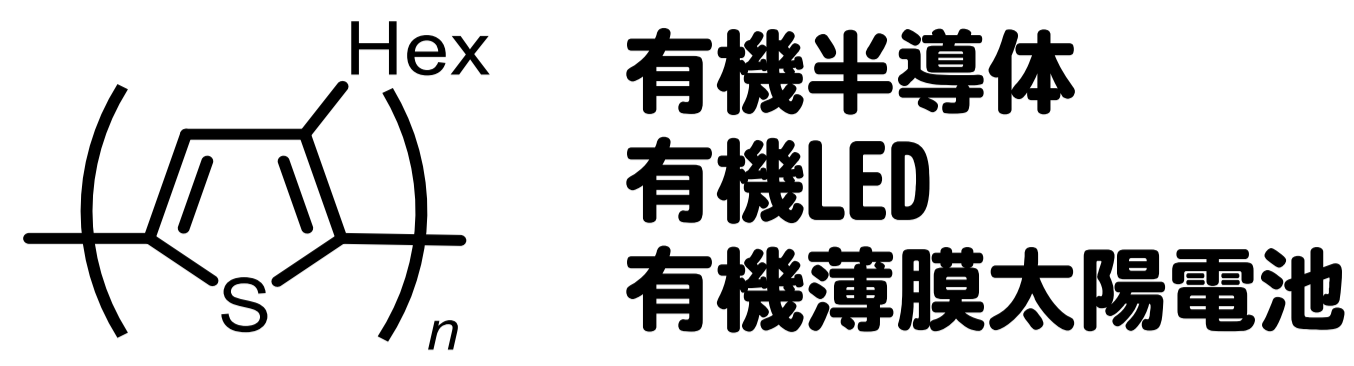


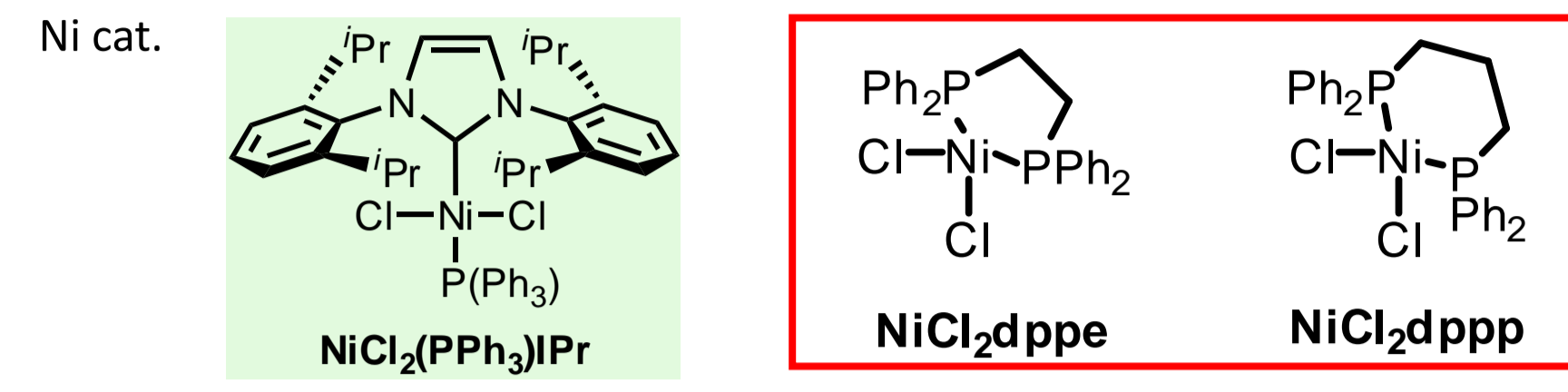
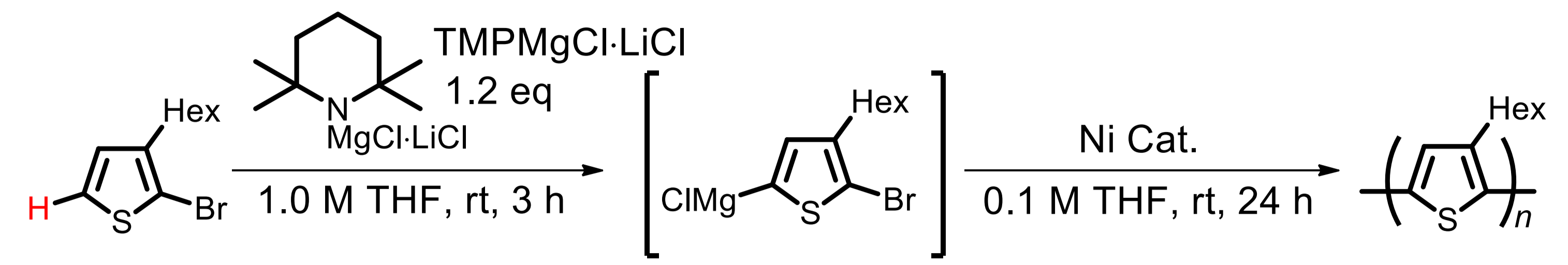
Background

◇ Poly(3-hexylthiophene) (P3HT)



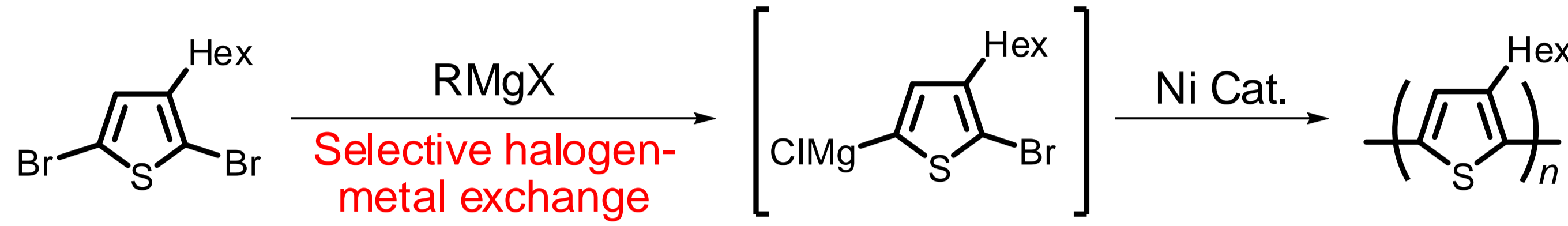
高性能材料

◇ 当研究グループ開発のポリチオフェン合成 C-Hカップリング重合



J. Am. Chem. Soc. **2011**, *133*, 9700–9703.
Chem. Lett. **2011**, *40*, 398–399.

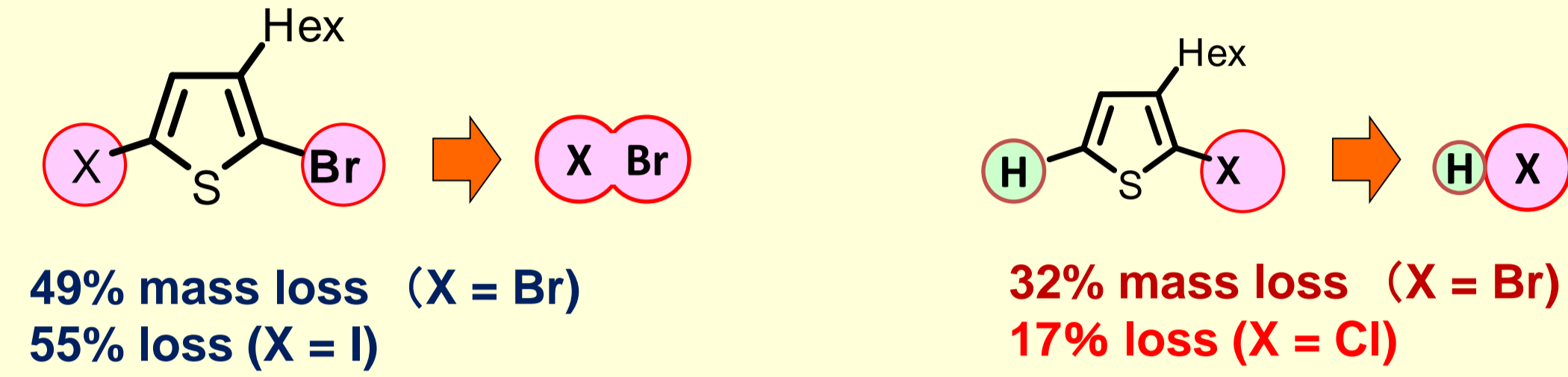
◆ 一般的なポリチオフェンの合成法 GRIM法



Rieke (USA), McCullough (USA), 横澤 (神奈川大)

Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202.

◆ ポリチオフェン合成の原子効率

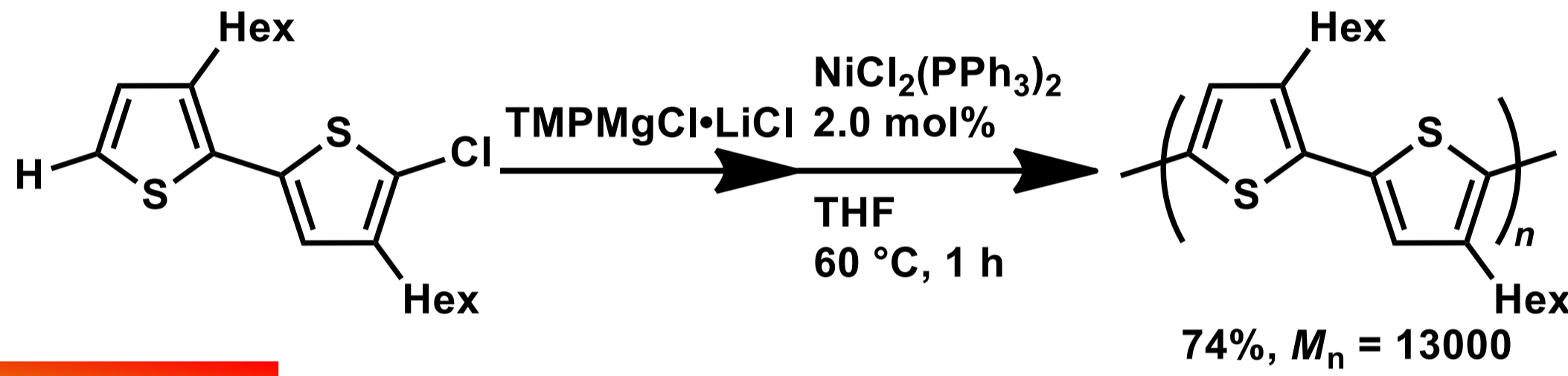


100 g 原料 (モノマー前駆体) から
 最高 80 g 以上のポリマー

Results & Discussion

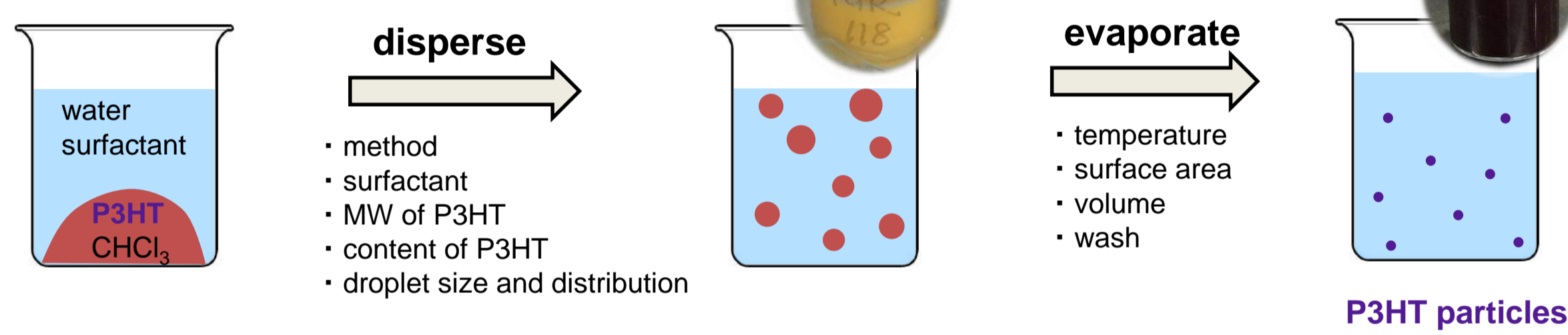
◆ This work

Polymerization of bithiophene as a monomer



Polythiophene particle

Solvent Releasing Method (SRM)

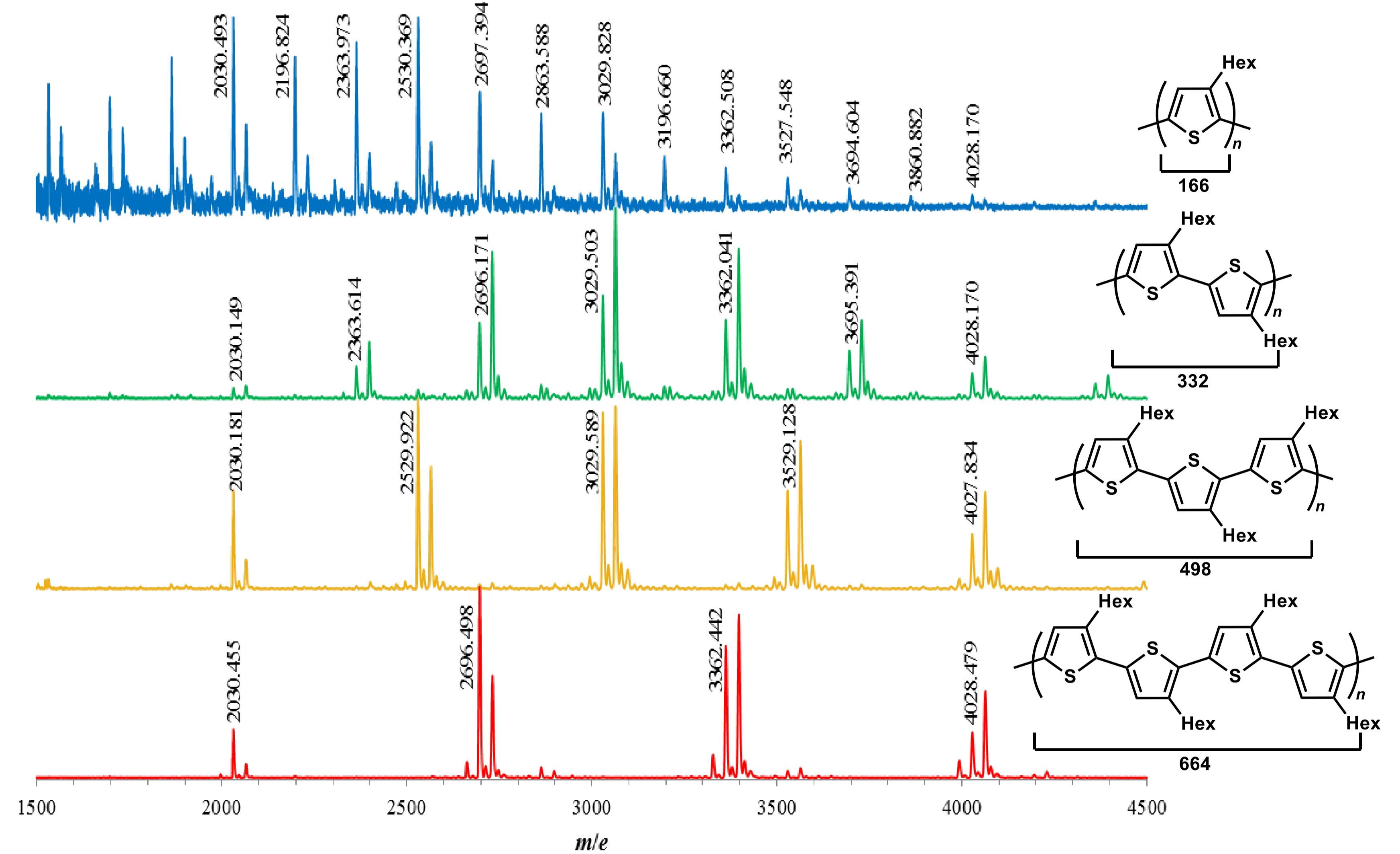


◆ Polymerization of bithiophene

| entry | catalyst | ligand | yield [%] | $M_n \times 10^{-3}$ | M_w/M_n |
|-------|---|------------------------------------|-----------|----------------------|-----------|
| 1 | NiCl ₂ (PPh ₃) ₂ | | 74 | 13.0 | 1.67 |
| 2 | NiCl ₂ (PPh ₃) ₂ ^a | | 69 | 13.0 | 1.48 |
| 3 | NiCl ₂ dppp | | 81 | 17.2 | 1.48 |
| 4 | NiCl ₂ (PPh ₃)IPr | | 84 | 39.0 | 1.67 |
| 5 | NiCl ₂ (dme) | 2.5 P(<i>o</i> -tol) ₃ | 2 | 8.5 | 1.30 |
| 6 | NiCl ₂ (dme) | 2.5 P(OEt) ₃ | 40 | 17.7 | 1.75 |
| 7 | NiCl ₂ (dme) | BPY | <1 | 6.9 | 1.23 |
| 8 | Ni(acac) ₂ | 5 PPh ₃ | 70 | 14.7 | 1.74 |
| 9 | PdCl ₂ (PPh ₃) ₂ | | <1 | -- | -- |
| 10 | PdCl ₂ dppe | | <1 | 8.9 | 1.49 |
| 11 | Pd-PEPPSI-SIPr | | 28 | 5.7 | 1.15 |

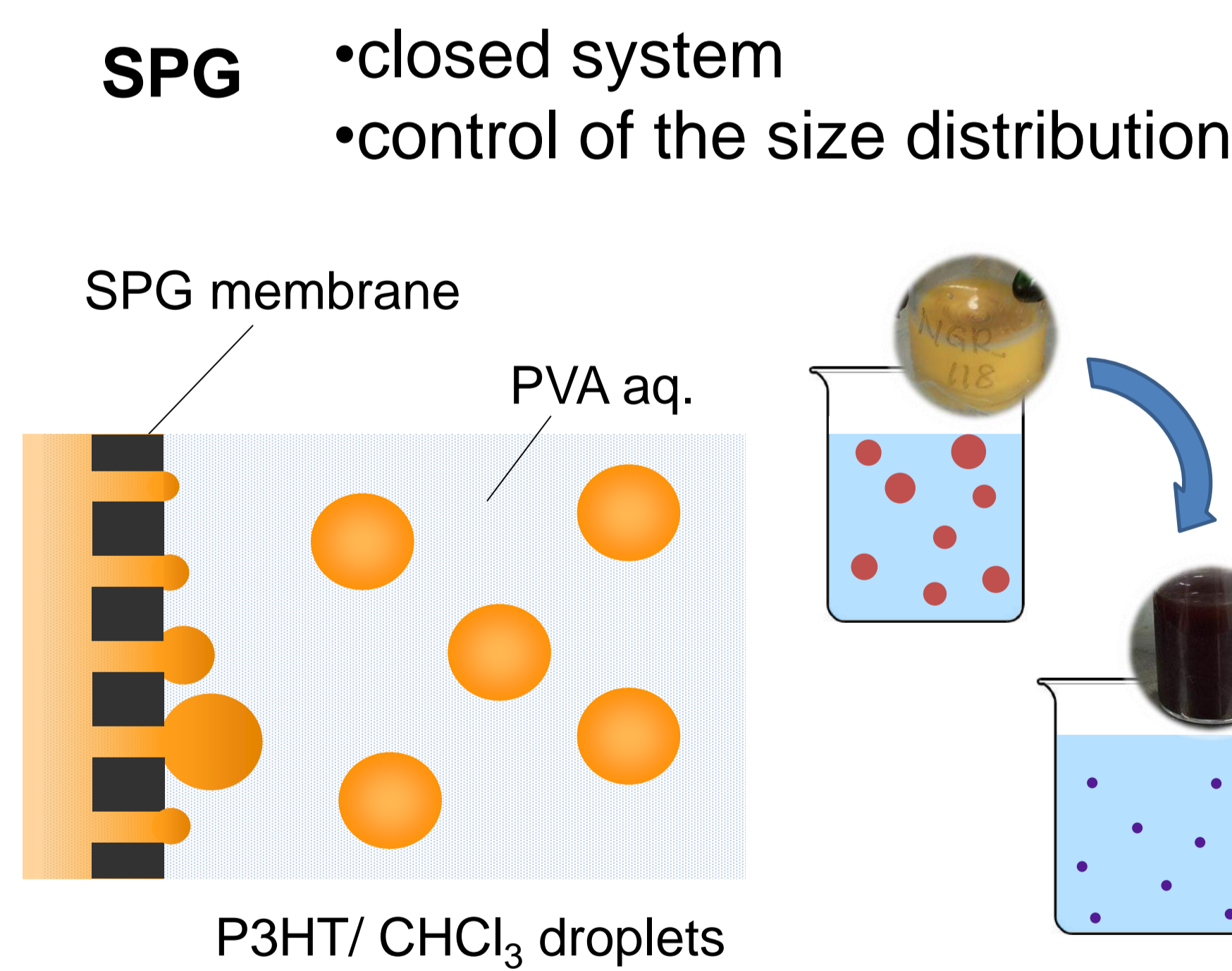
^a The polymerization was carried out at r.t. for 3 h.

◆ MALDI-TOF mass spectra of poly(3-hexylthiophene)



◆ Preparation of P3HT particle

Preliminary result



P3HT/CHCl₃ droplets (0.5 wt%)
 with PVA as surfactant

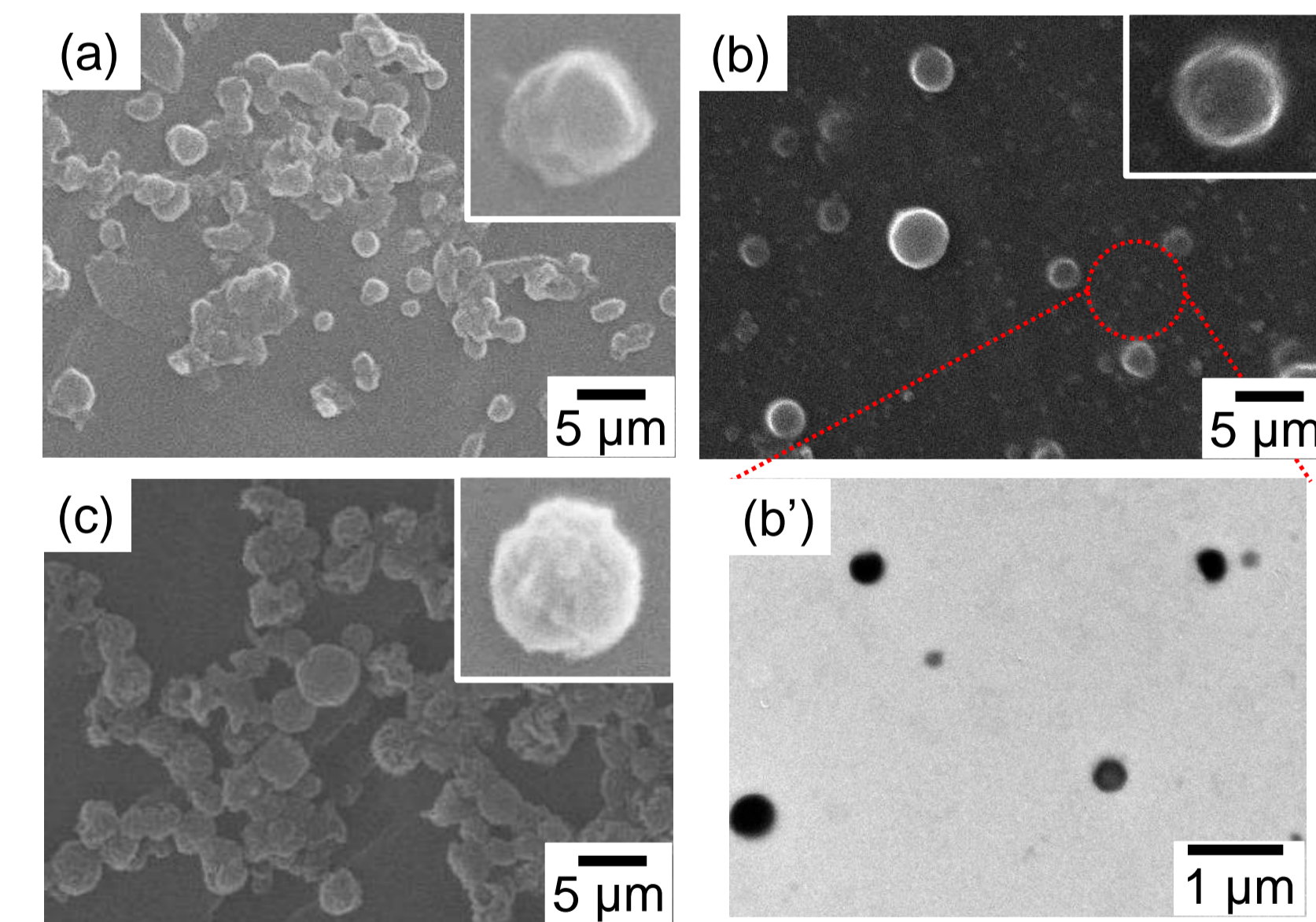
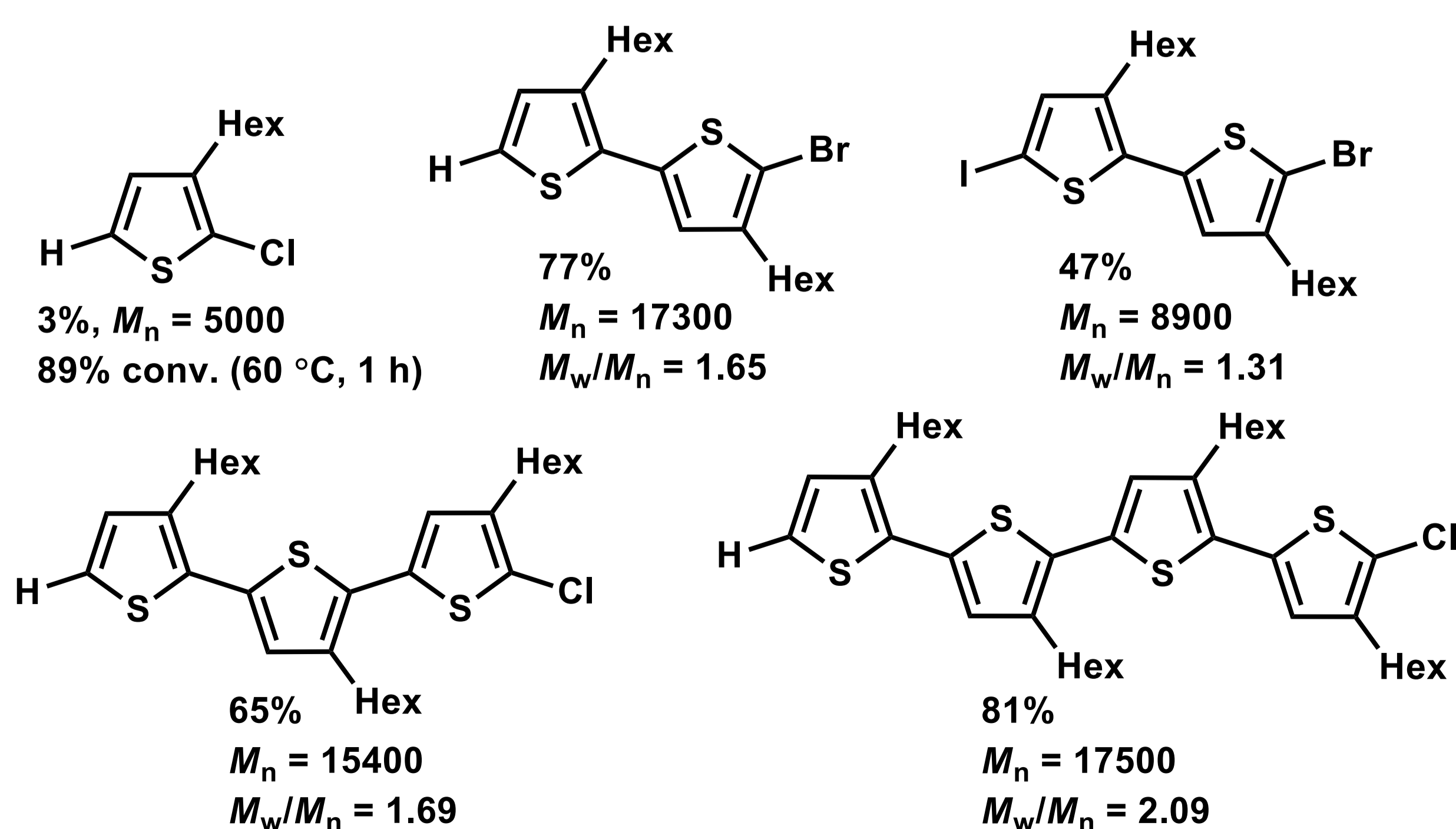


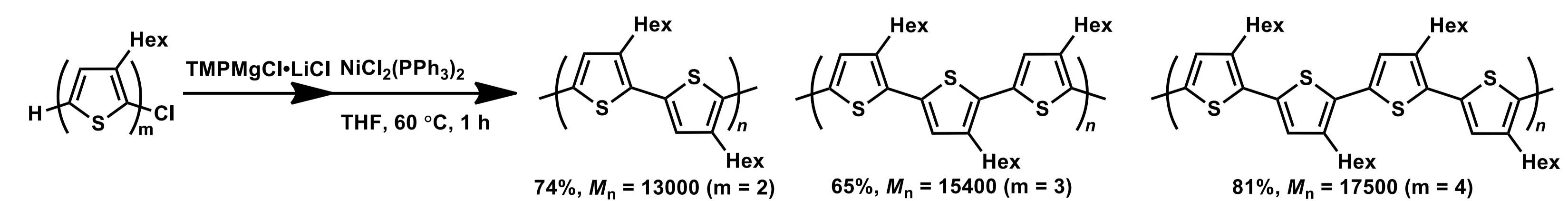
Fig. SEM (a-c) and TEM (b') images of P3HT particles prepared by solvent releasing method from the droplets of 0.5% P3HT chloroform solution with PVA. MW of P3HT: (a) 7,000, (b) 20,000, (c) 50,000.

◆ Polymerization of bithiophene derivatives with NiCl₂(PPh₃)₂ as a catalyst

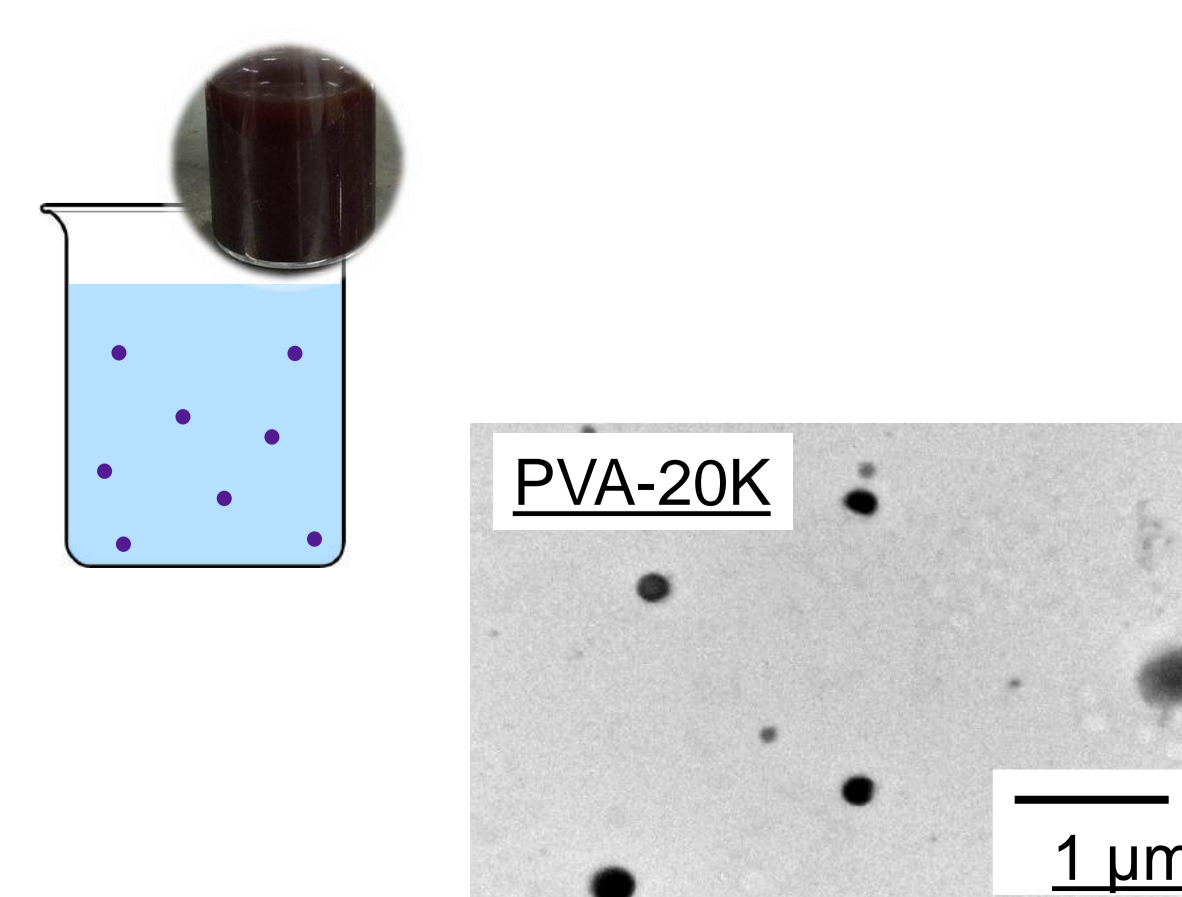


Summary

◆ Ubiquitous and less reactive catalyst, NiCl₂(PPh₃)₂, effectively catalyzes polymerization of thiophene oligomers.



◆ Polythiophene particles



◆ Prospects
 Siloxane-containing polyT soluble in hexane
 特開 2013-160864
 Chem. Lett. 2014
 Macromolecules 2015

77
 15T