Through-Space Conjugated Polymers and Conjugated Main-Chain Metallopolymers

Wednesday seminar

Gang Li

12/2/2015

Conjugated Polymer Synthesis. Edited by Yoshiki Chujo

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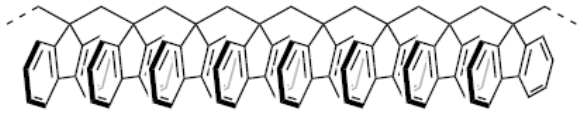
Through-Space Conjugated Polymers

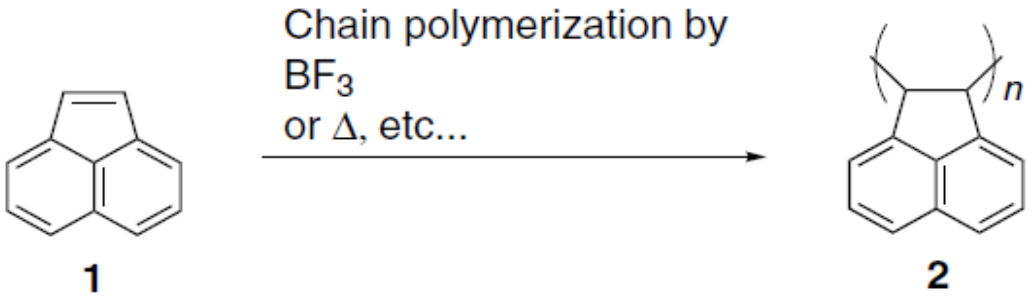
- Yasuhiro Morisaki and Yoshiki Chujo

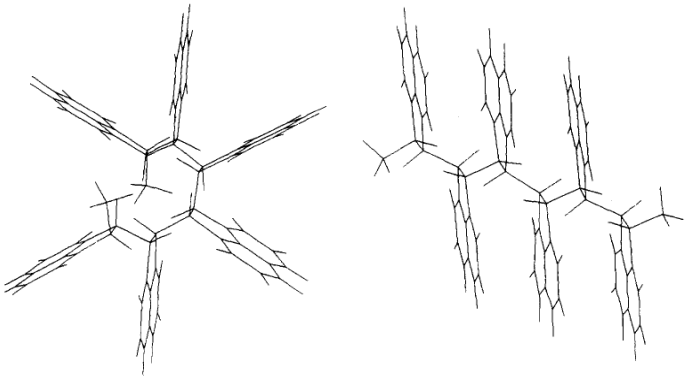
•Through-space conjugated polymers are π-stacked polymers in which π-electron systems such as aromatic rings or π-electron systems are layered in the single polymer chain.

•It is worth noting that layered π-electron systems are commonly found in nature. Such as layered aromatic rings in DNA .



Synthesis of Polyacenaphthylene



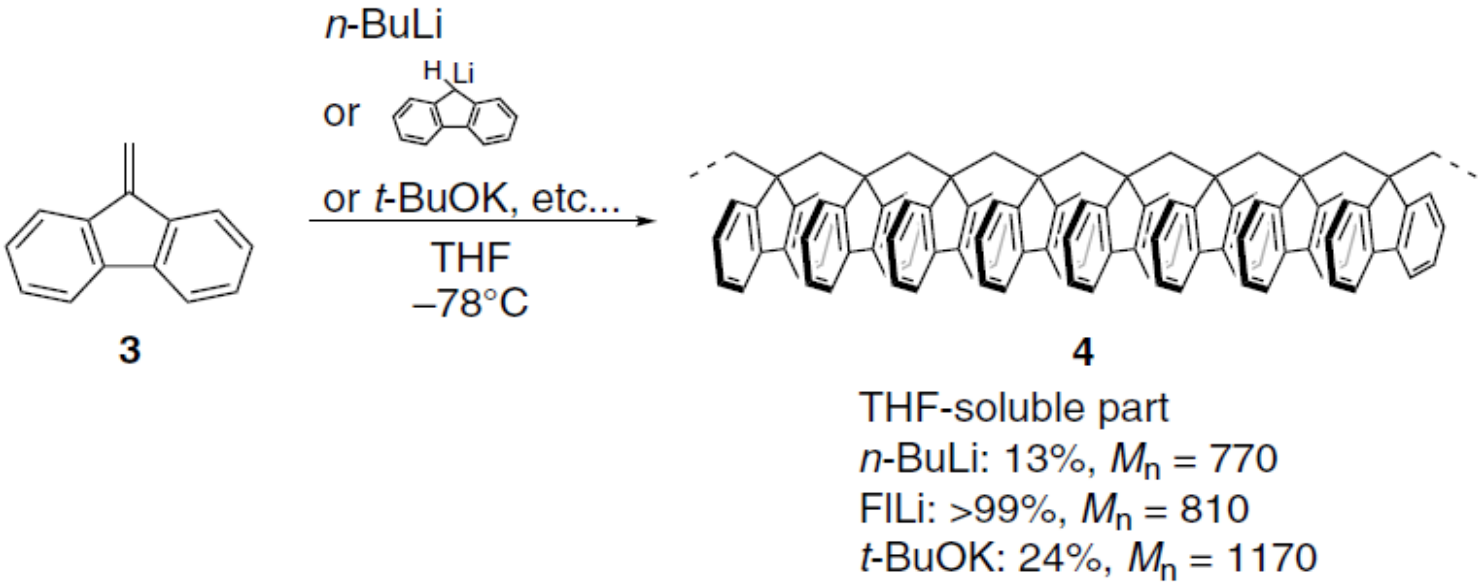


•**The polyacenaphthylene in diluted solution showed photoluminescence from monomer units and intramolecular excimers, depending on the stereoregularity**

Wang, Y.-C. Morawetz, H. *Makromol. Chem. Suppl.*,**1975**, *1*, 283–295

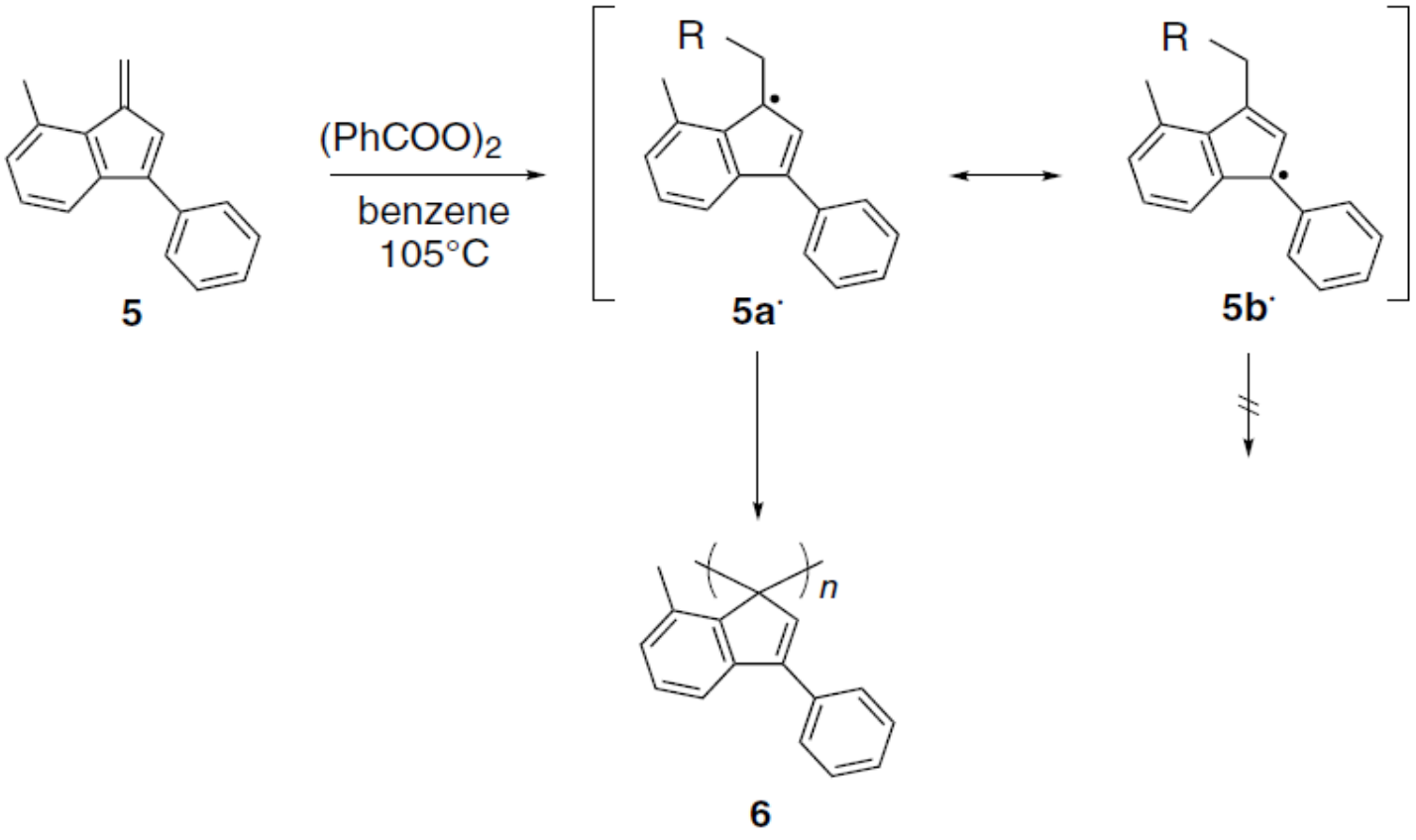
Mendicuti, F., Kulkarni, R., Patel, B., Mattice, W.L. *Macromolecules*, **1990**, *23*, 2560–2566

Through-Space Conjugated Polymers with the Layered π-Electron Systems in the Side Chain



Nakano, T., Takewaki, K., Yade, T., and Okamoto, Y. *J. Am. Chem. Soc*., **2001,** *123*, 9182–9183; Nakano, T. and Yade, T. *J. Am. Chem. Soc*., **2001**, *125*,15474–15484;

Synthesis of Polybenzofulvene



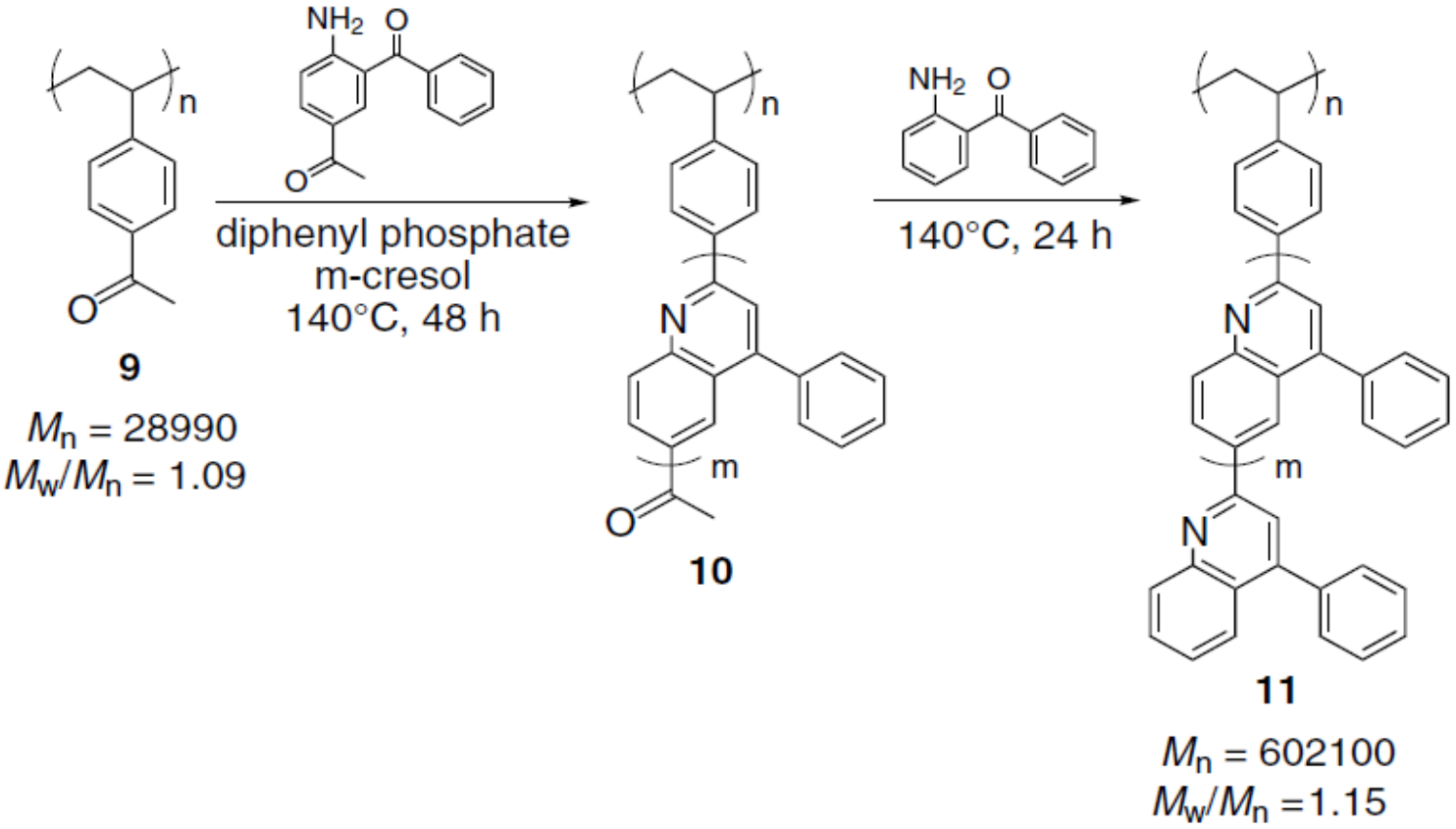
5 **5a**· **5b**·

6

75%, M_n = 13800, M_w = 64700

Londergan, T.M., Teng, C.J., and Weber, W.P. *Macromolecules*, **1999**, *32*, 1111–1114

Polystyrene-graft-Poly(4-Phenylquinoline)

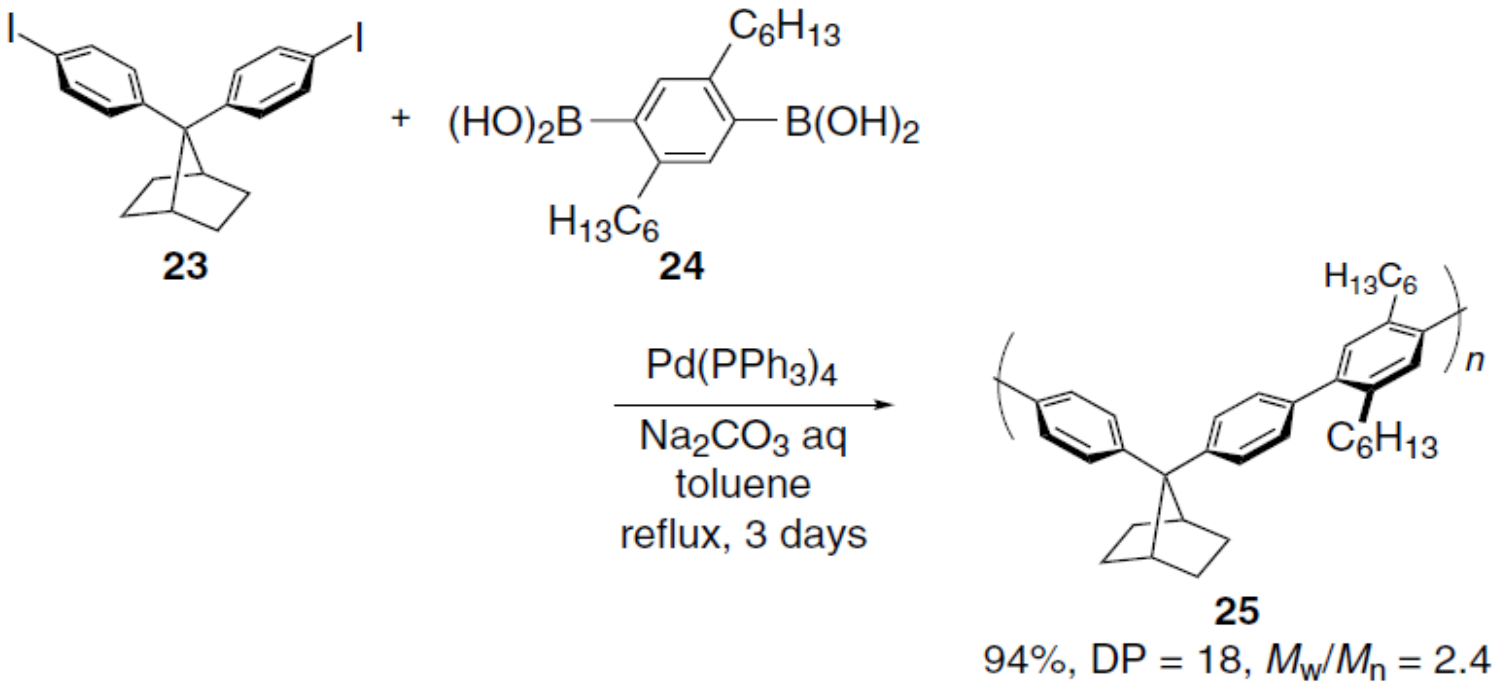


•An electroluminescence (EL) device using polymer 11 as an emitting layer showed increasing efficiency and brightness

Jenekhe, S.A., Alam, M.M., Zhu, Y., Jiang, S., and Shevade, A.V. *Adv. Mater*., **2007**, *19*, 536–542

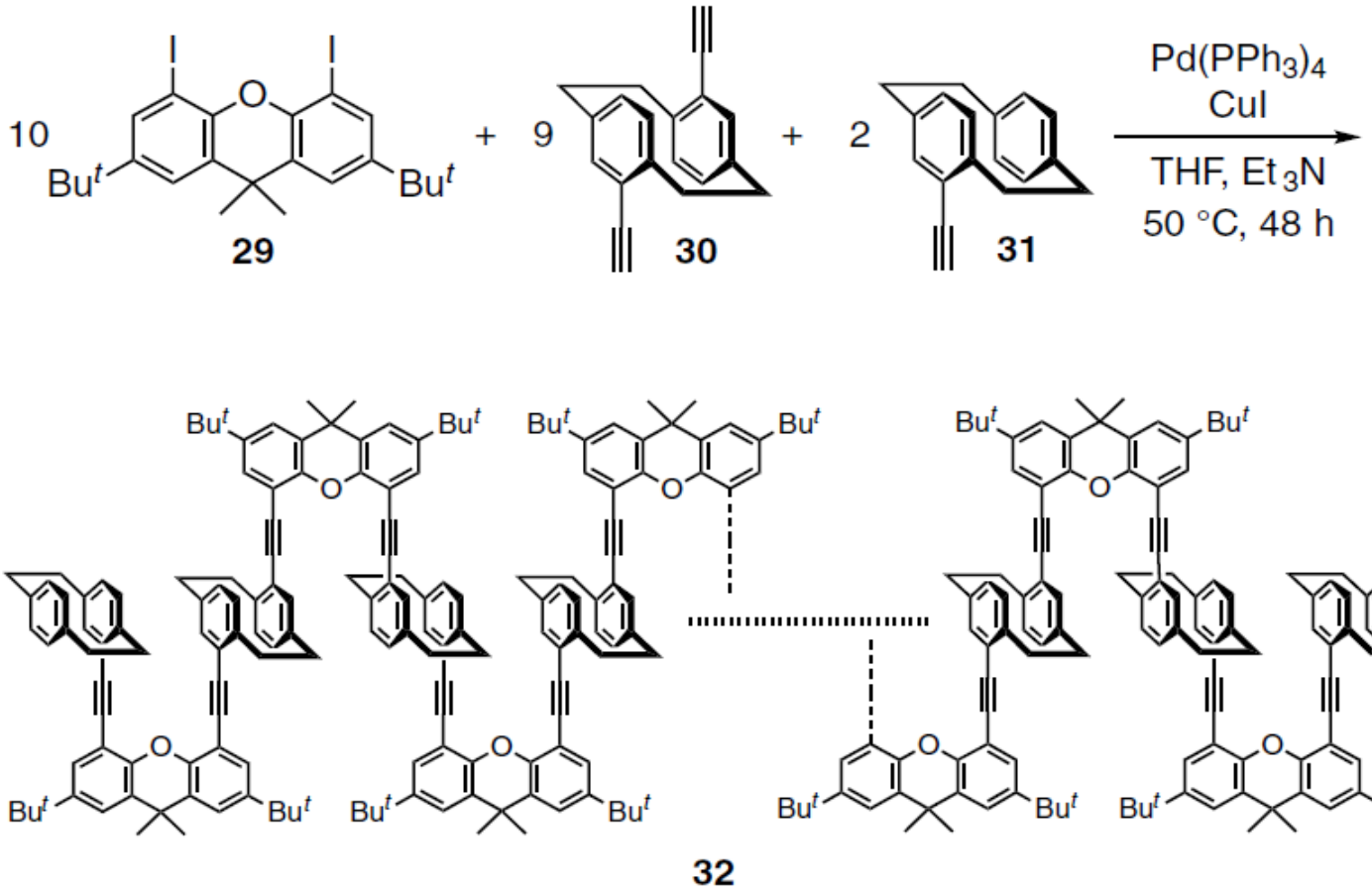
Through-Space Conjugated Polymers with the Layered π-Electron Systems in the main Chain

- **Phenylene-Layered Polymer Based on a Norbornane Scaffold**



Garcıa Martınez, A., et al. *Adv. Mater.*, **1999**, *11*, 27–31;

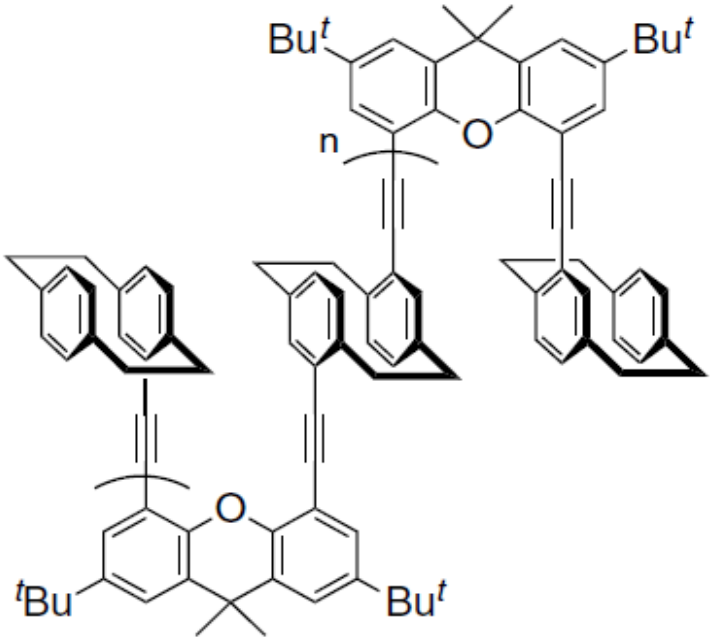
Aromatic Ring-Layered Polymers Based on a Xanthene Scaffold



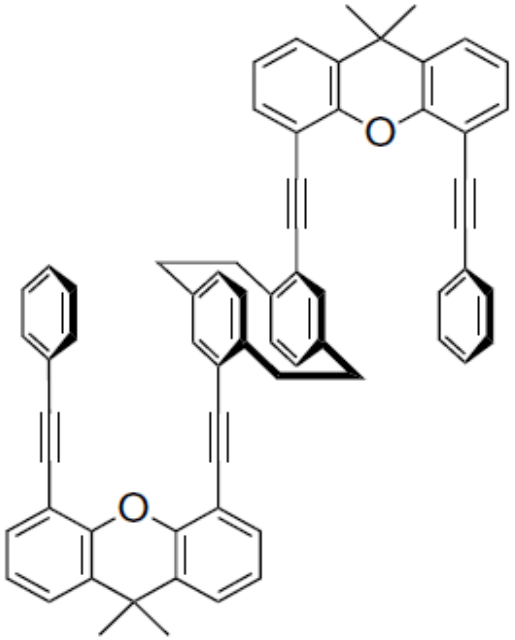
Mn: 4100. Sixteen benzenes were layered in the polymer main chain.

Morisaki, Y.,Murakarni, T., Chujo, Y. *Macromolecules*, **2008**, *41*, 5960–5963

Aromatic Ring-Layered Polymers Based on a Xanthene Scaffold

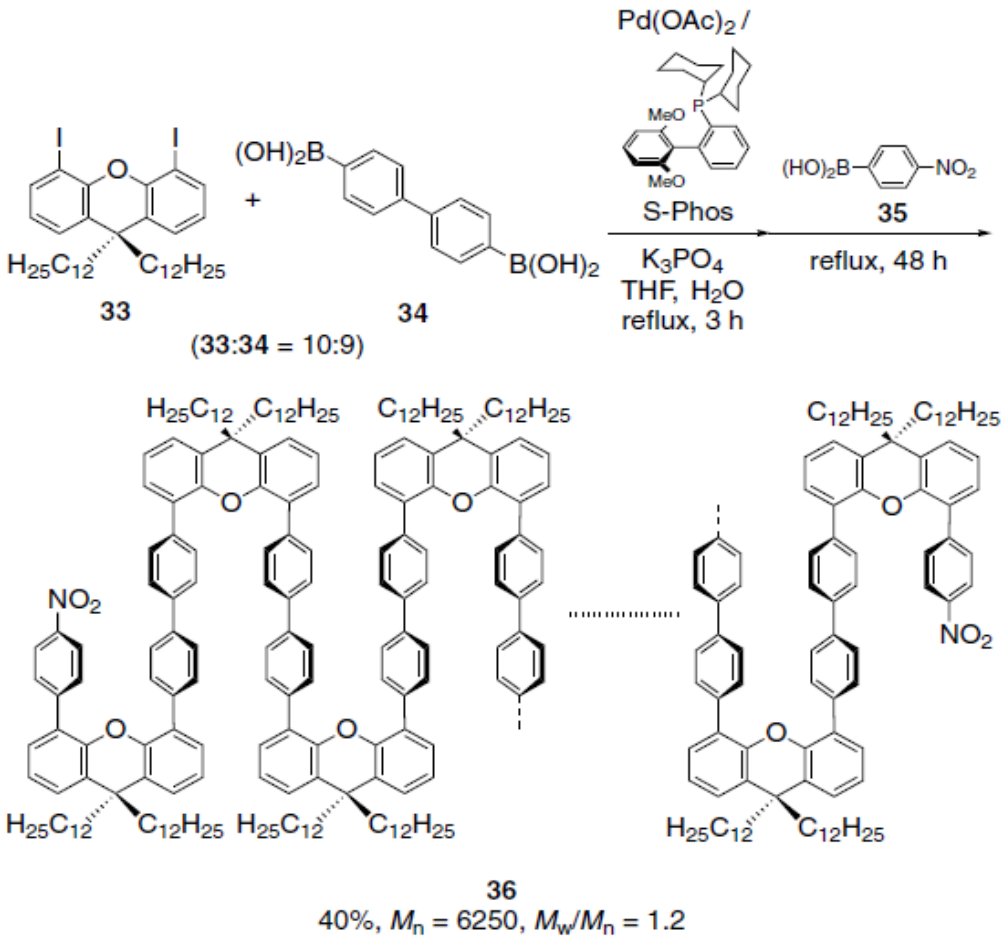


32a (M_n = 4100): $\lambda_{abs,max}$ = 330 nm
32b (M_n = 3100): $\lambda_{abs,max}$ = 330 nm
32c (M_n = 2100): $\lambda_{abs,max}$ = 330 nm



33 $\lambda_{abs,max}$ = 320 nm

Oligophenylene-Layered Polymers

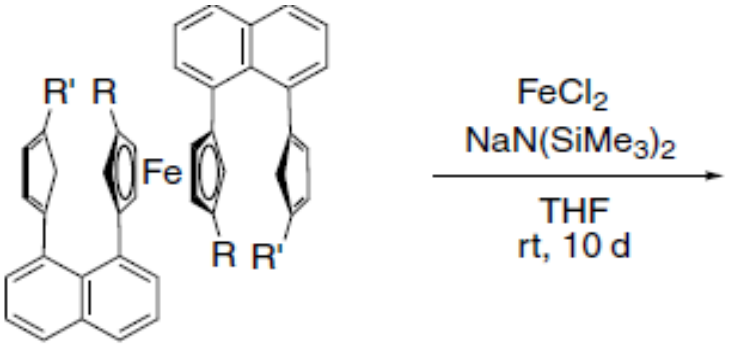


•The two end capping nitrobenzene units in polymer 36 effectively quenched the photoluminescence of the layered biphenylenes

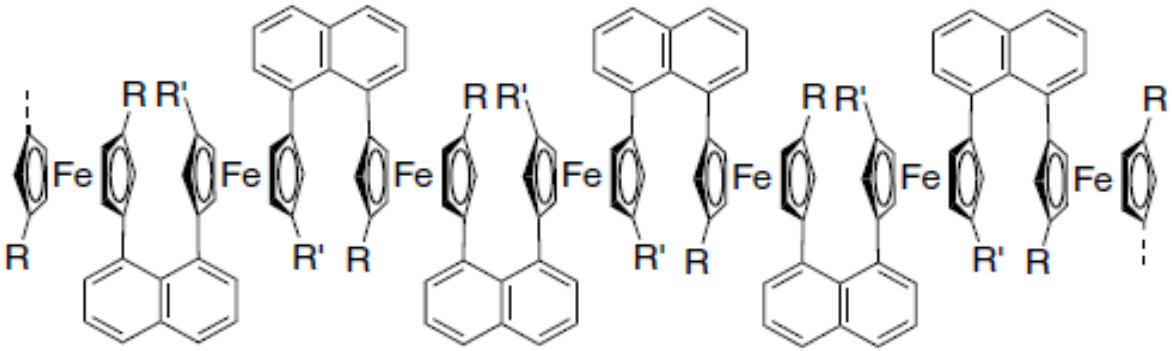
Morisaki, Y., Imoto, H., Miyake, J., Chujo, Y. *Macromol. Rapid Commun*., **2009,** *30*, 1094–1100.

Ferrocene-Layered Polymers Based on a Naphthalene Scaffold

Synthesis of Face- to-Face Metallocene Polymers



37



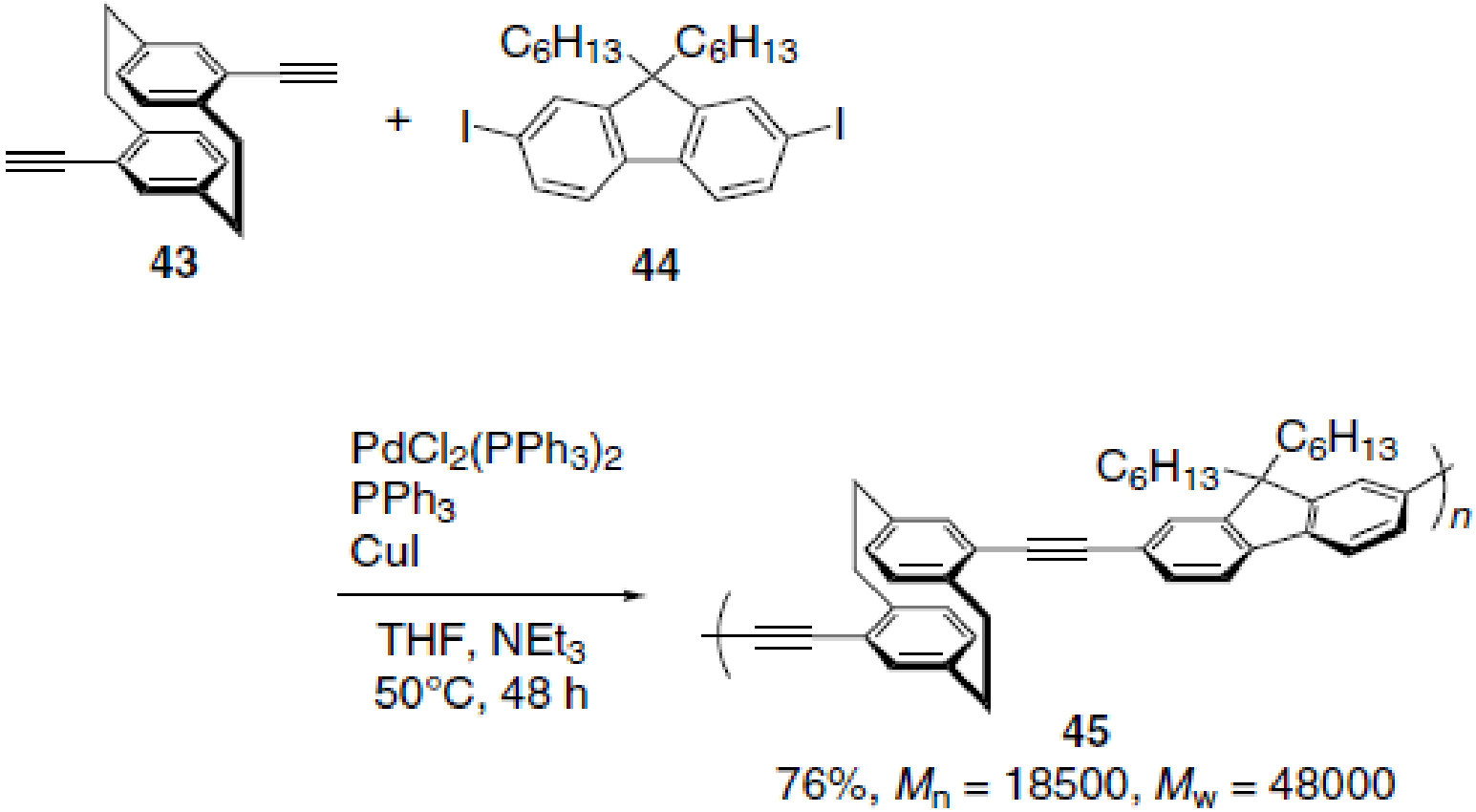
38

R = 2-octyl, R' = H: 71%, M_n = 18000 (by ^{1}H NMR)
R, R' = 2-octyl: 40%, M_n = 139000 (by GPC)

Nugent, H.M., Rosenblum, M., and Klemarczky, P. *J. Am. Chem. Soc*., **1993**, *115*, 3848–3849; Rosenblum, M., et al. *Macromolecules*, **1995**, *28*, 6330–6342

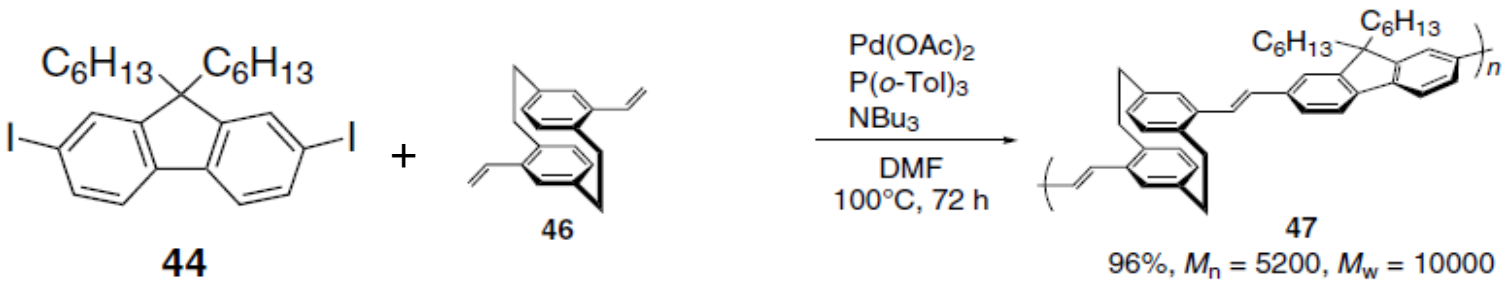
[2.2]Paracyclophane-Containing Through-Space Conjugated Polymers

•**Synthesis of [2.2]paracyclophane-containing poly(p-arylene-ethynylene) 45 by the Sonogashira–Hagihara reaction.**



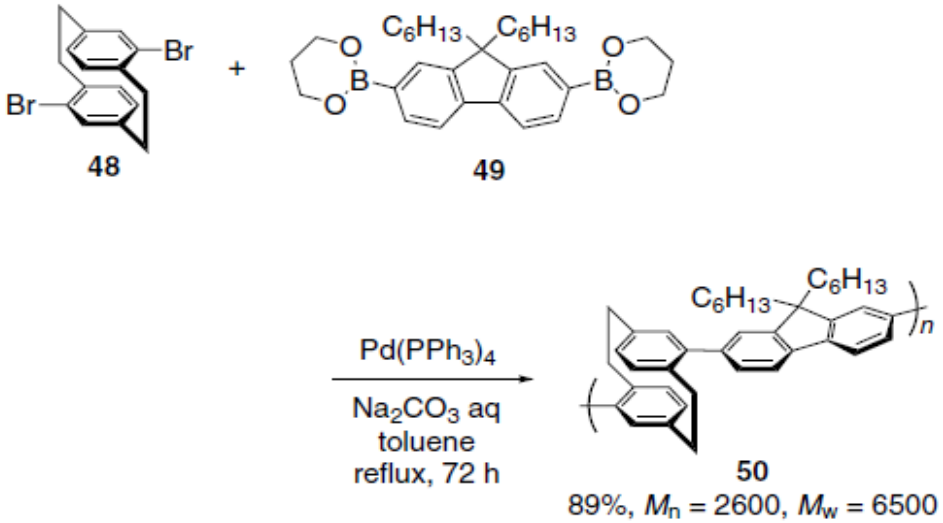
Morisaki, Y. and Chujo, Y. *Chem. Lett.*, **2002**, 194–195;

•**by the Heck reaction.**



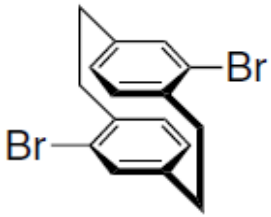
Mitchell, R.H. *J. Am. Chem. Soc.*, **2002**, *124*, 2352–2357.

•**by the Suzuki-Miyaura reaction**

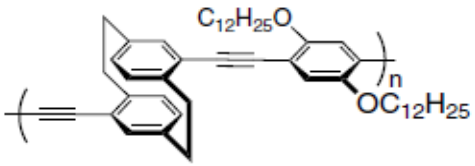


Morisaki, Y. and Chujo, Y. *Bull. Chem. Soc. Jpn.*, **2005,** 78, 288–293

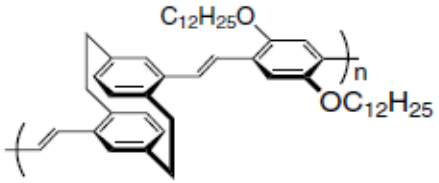
Several examples



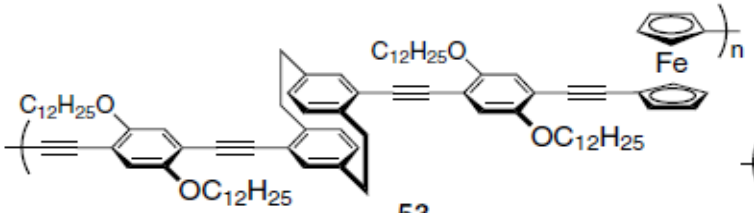
The key monomer



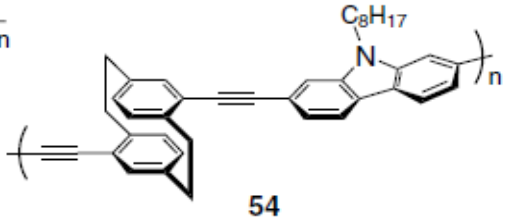
51
M_n = 14500, M_w = 35500



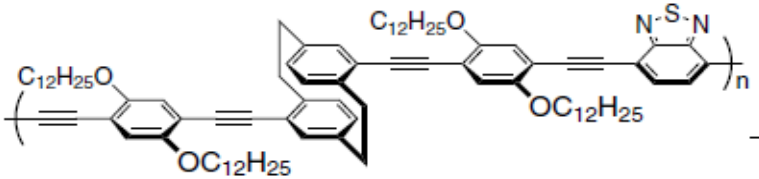
52
M_n = 4200, M_w = 8300



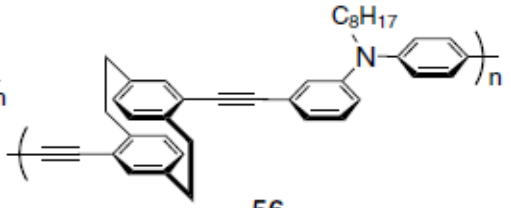
53
M_n = 24500, M_w = 66300



54
M_n = 4400, M_w = 8500



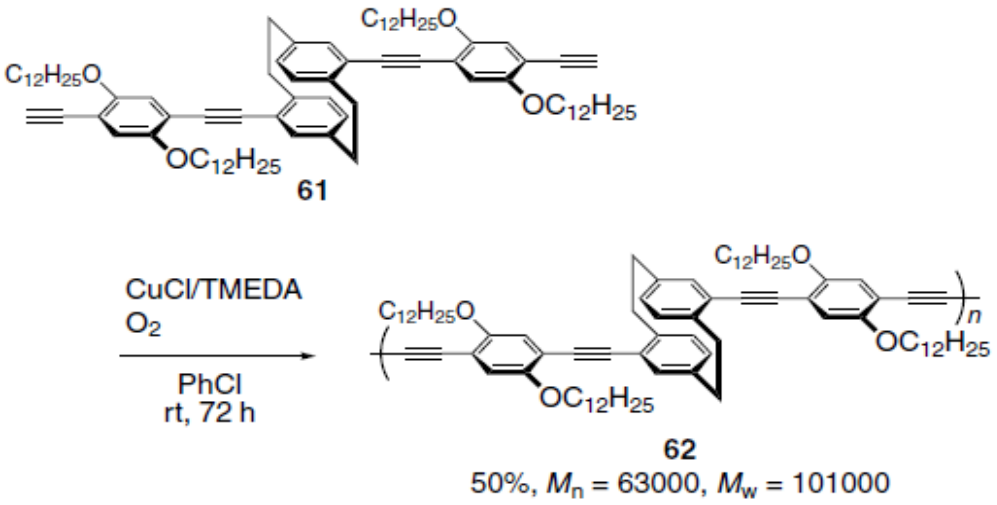
55
M_n = 29700, M_w = 76800



56
M_n = 4300, M_w = 13300

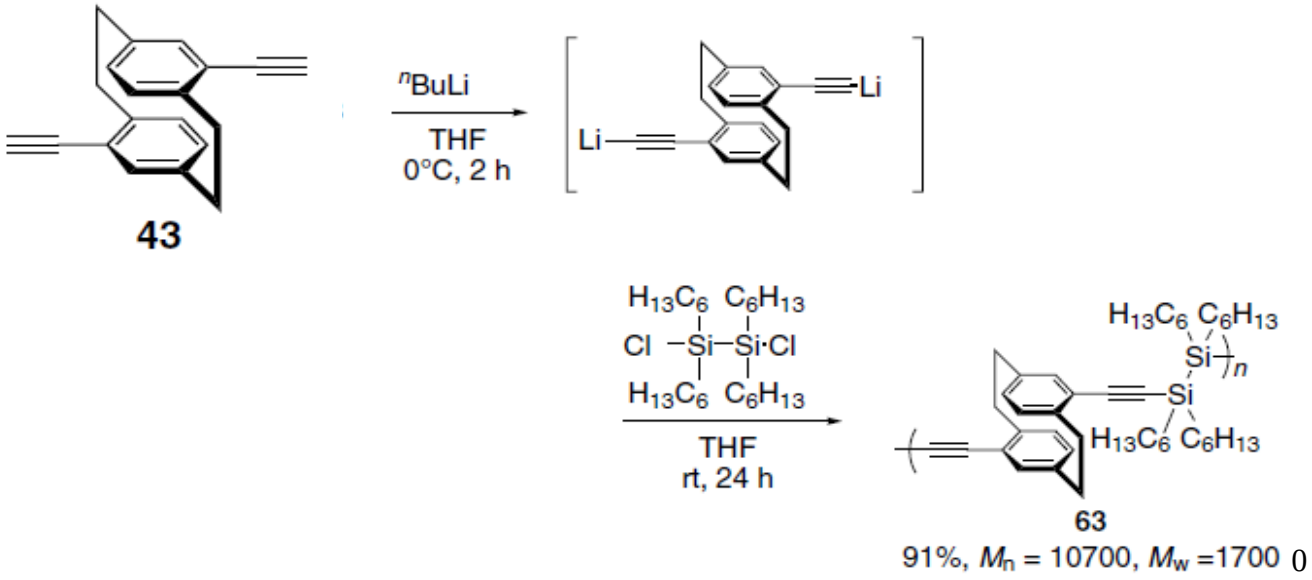
a) Morisaki, Y. and Chujo, Y. *Macromolecules*, 2002 *35*, 587–589; (b) Morisaki, Y., Ishida, T., and Chujo, Y. *Macromolecules*, **2002**, 35, 7872–7877; (c) Morisaki, Y. and Chujo, Y. M*acromolecules*, **2003,** *36*, 9319–9324

The oxidative coupling reaction



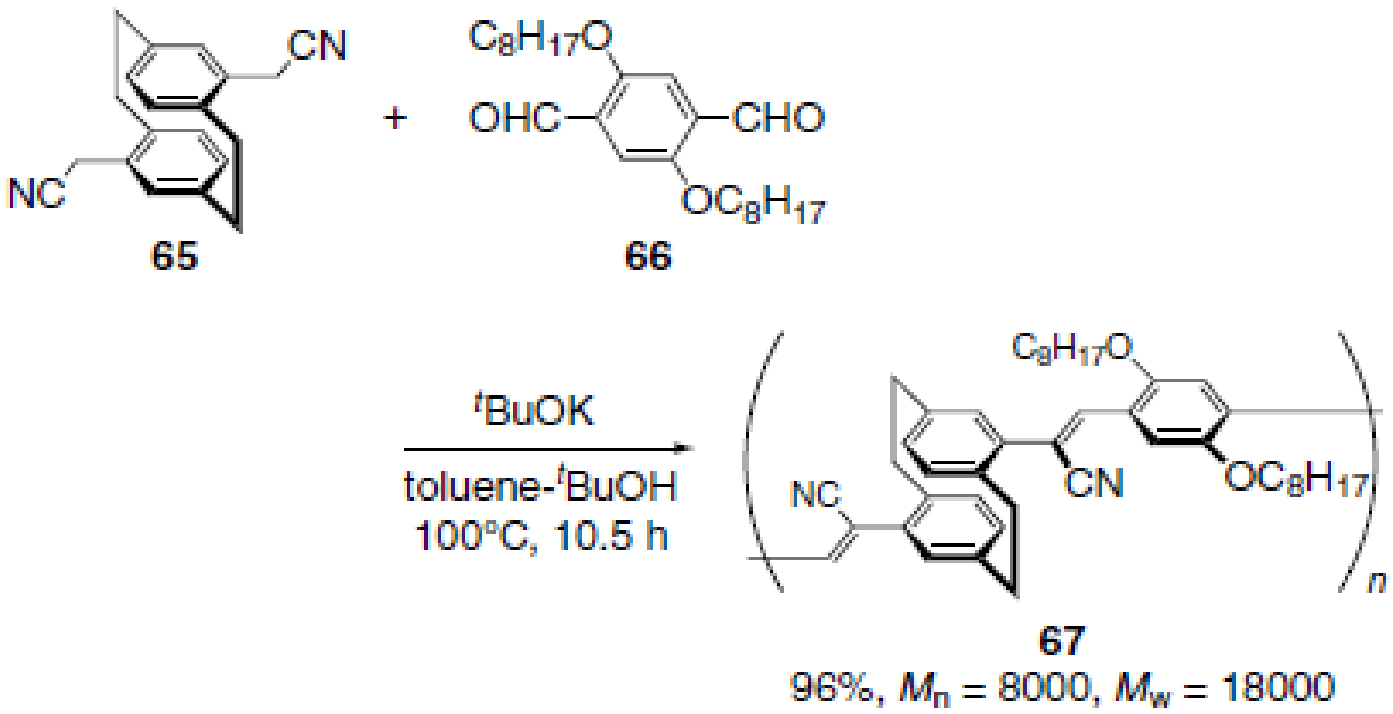
Morisaki, Y. and Chujo, Y. *Polym. Bull.*, **2002**, *49*, 209–215

Conjugated polymer comprising disilylene and [2.2]paracyclophane units



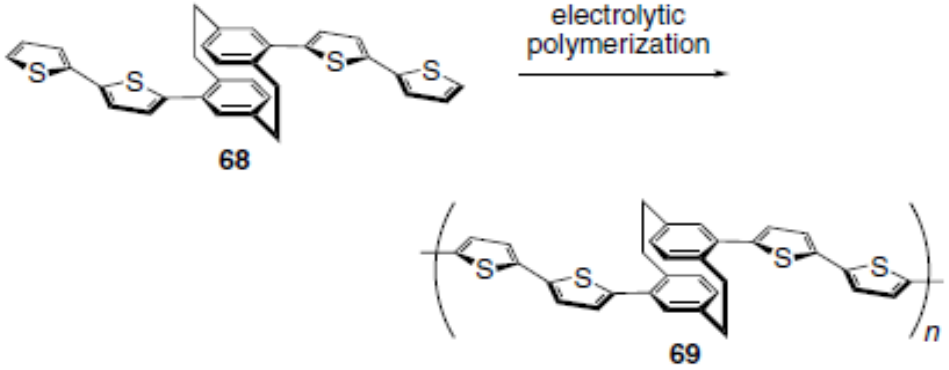
Morisaki, Y., Fujimura, F., and Chujo, Y. *Organometallics*, **2003,** *22*, 3553–3557

Knoevenagel reaction

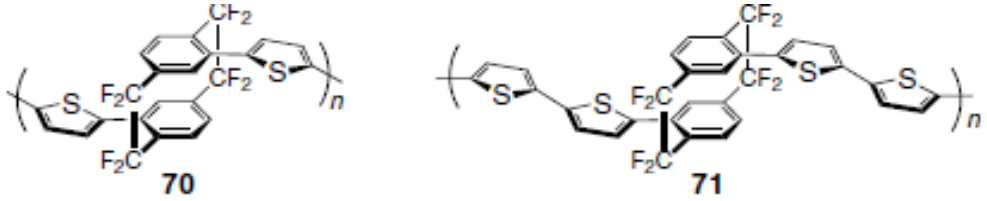


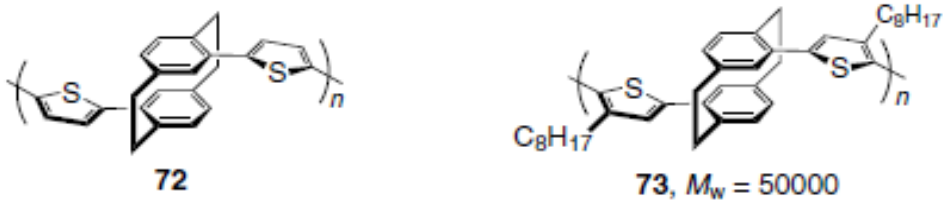
(a)Morisaki,Y., Lin, L., andChujo,Y. *Chem. Lett*., (**2009**) *38*, 734–735; (b) Morisaki, Y.,Lin, L., and Chujo, Y. *J. Polym. Sci. Part A: Polym. Chem*., (**2009**) *47*, 5979–5988.

•Electrochemical polymerization



Guyard, L. and Audebert, P. *Electrochem. Commun.*, **2001**, 3, 164–167





Salhi, F. and Collard, D.M. Adv. Mater., **2003,** 15, 81–85.

Applications:

- Through-space conjugated polymers can potentially be used as optoelectronic devices such as photovoltaic devices, and electroluminescence devices, as well as in a single molecule device . .

- # Synthetic Strategies to Conjugated Main-Chain Metallopolymers

Andreas Wild, Andreas Winter, Martin D. Hager, and Ulrich S. Schubert

•The great interest in these materials is mainly attributed to their special properties, which represent a combination of the physical, electronic and optical properties of the organic polymer as well as the physical, electronic and optical properties of the incorporated metal complexes
•Having many advantages compared to inorganic semiconductors, such as low cost, and the suitability for solution processing and large area application.

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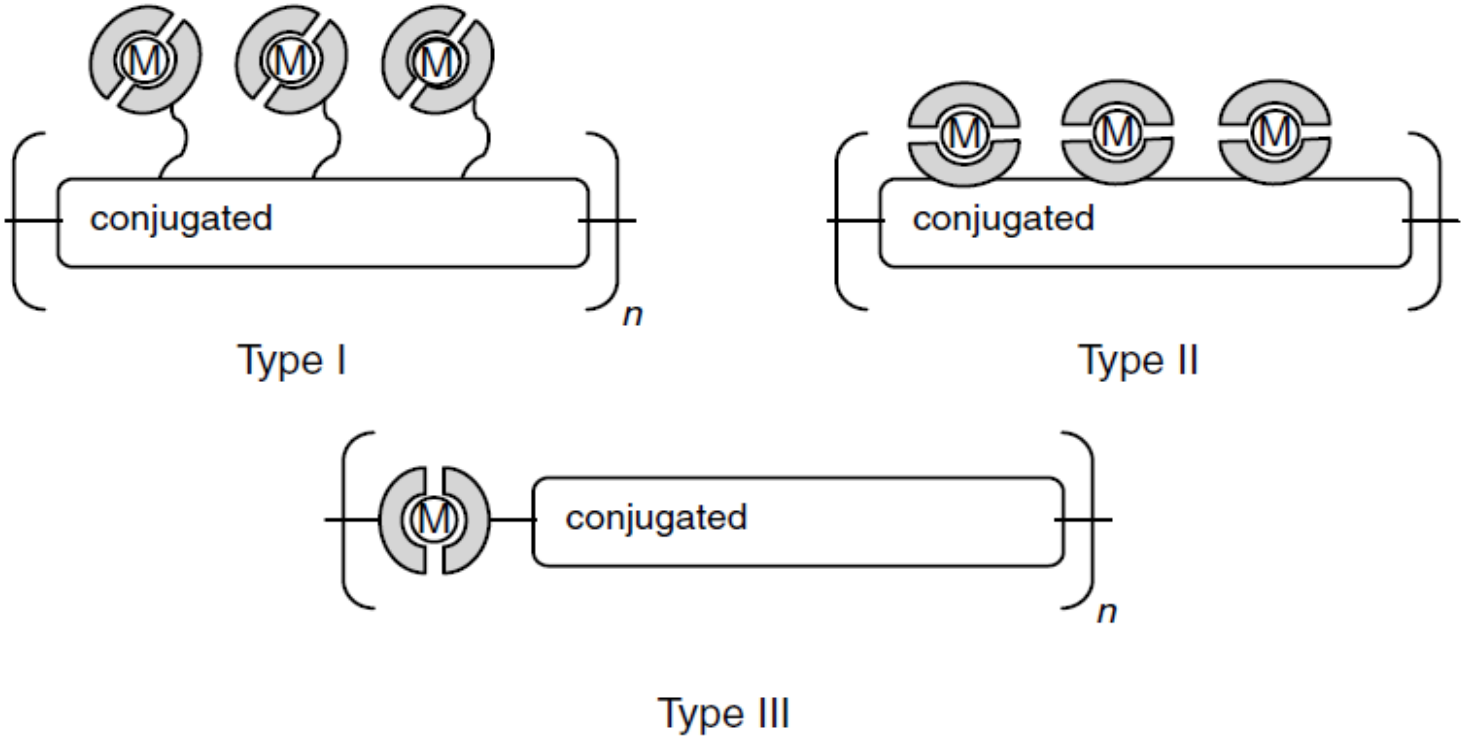
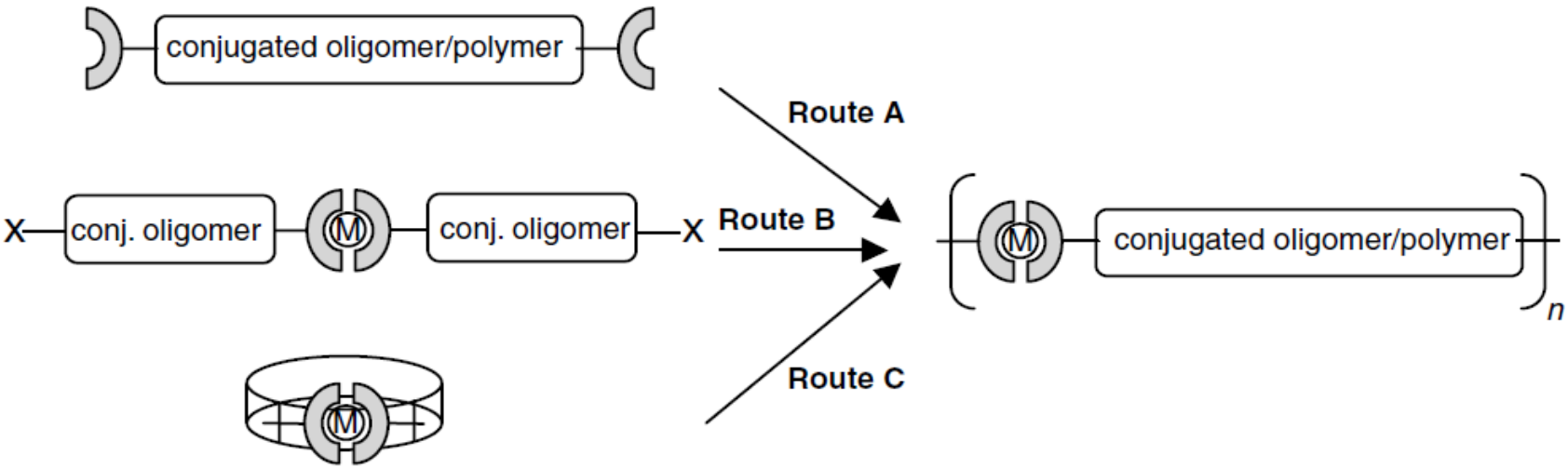
Three Different Types of Conjugated Metallopolymers



Wolf, M.O. *Adv.Mater.*, *13*, **2001**,545–553.

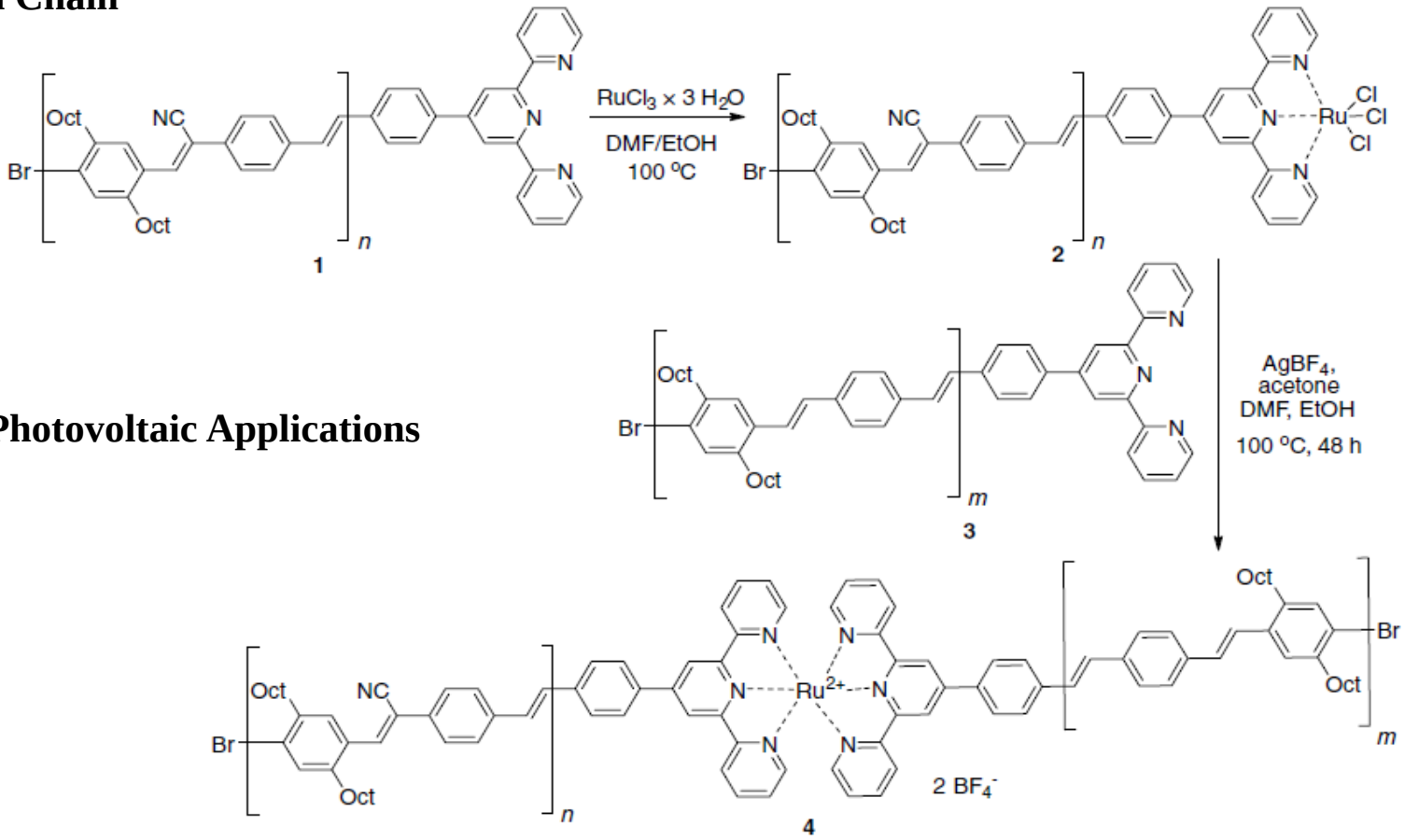
Synthetic Routes



•**Due to the broad field of different metallopolymers, my topic will mainly focus on conjugated metallopolymers with terpyridines, porphyrins and metallaynes**

Conjugated Metallopolymers with Terpyridines

•π-Conjugated Polymers with Terpyridine Units and Other Tridentate Ligands as Part of the Main Chain

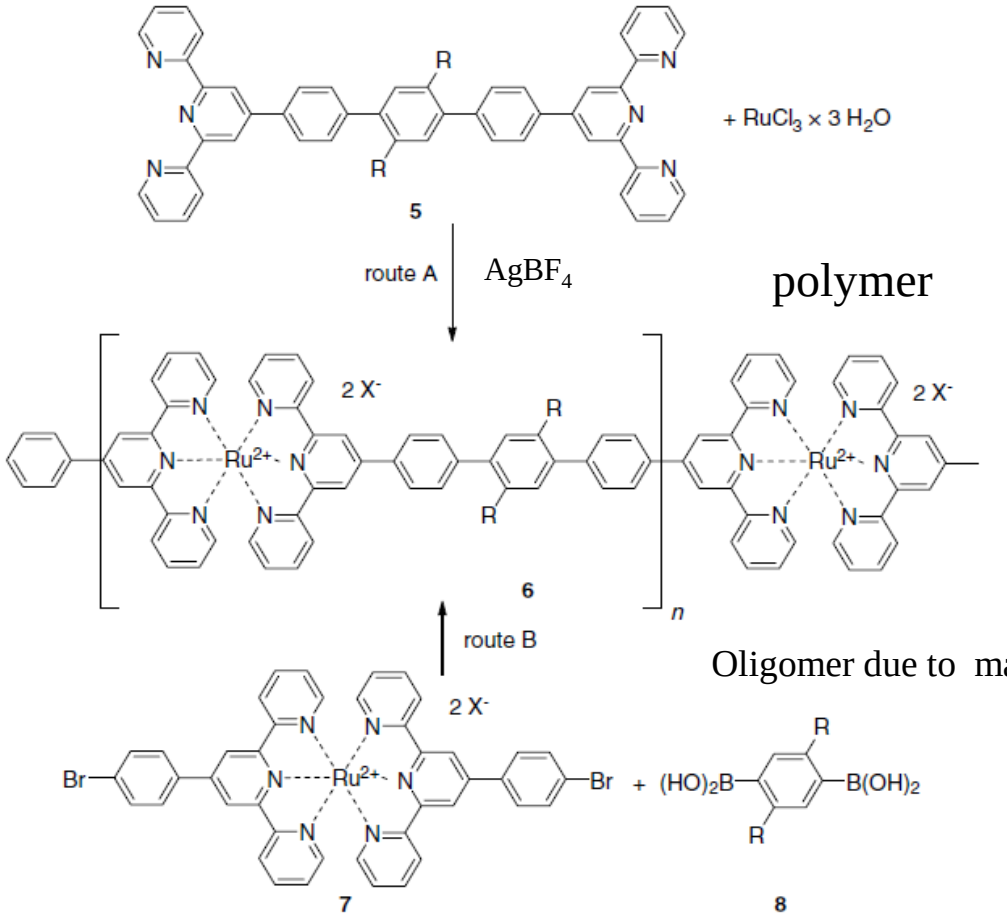


For Photovoltaic Applications

In this case, terpyridine plays only structural role.

Macromolecules **2005,** *38*, 10436-10448

Conjugated Metallopolymers with Terpyridines

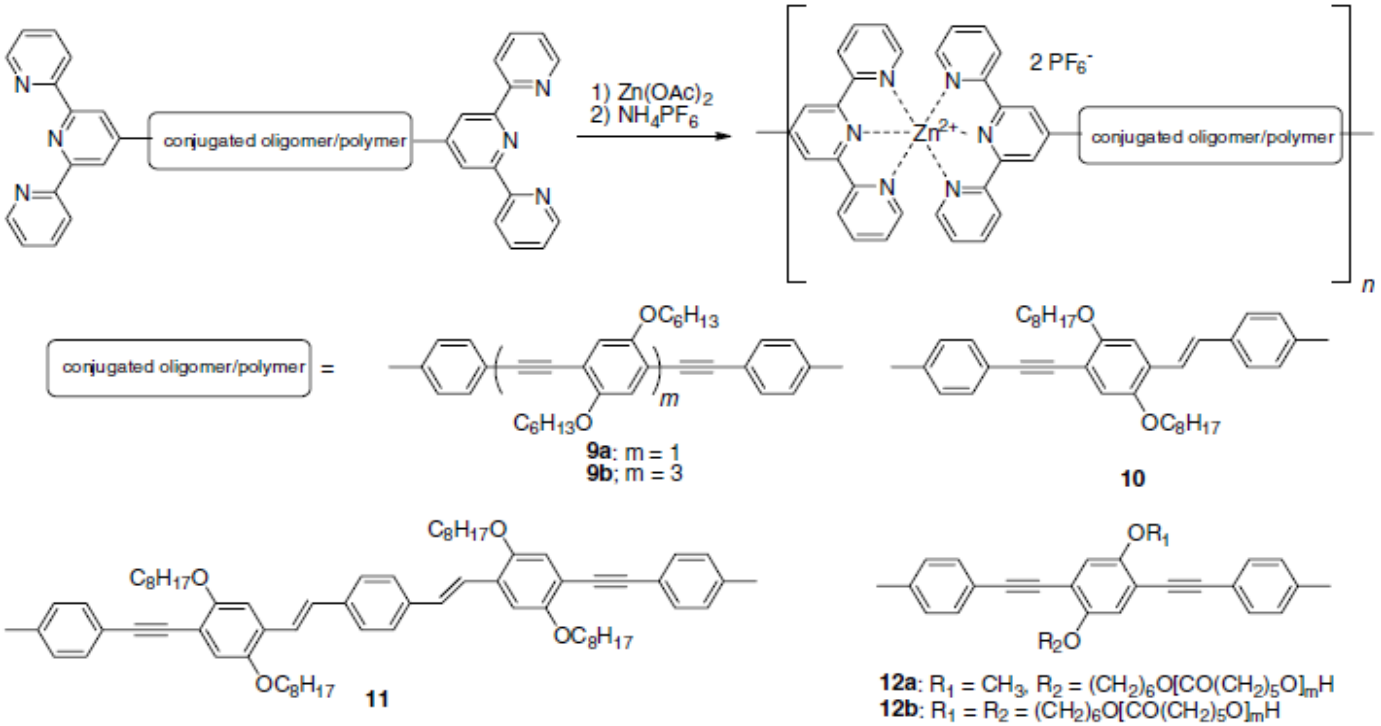


DP up to 30

Kelch, S.; Rehahn, M. *Macromolecules* **1999,** *32,* 5818-5828

Conjugated Metallopolymers with Terpyridines

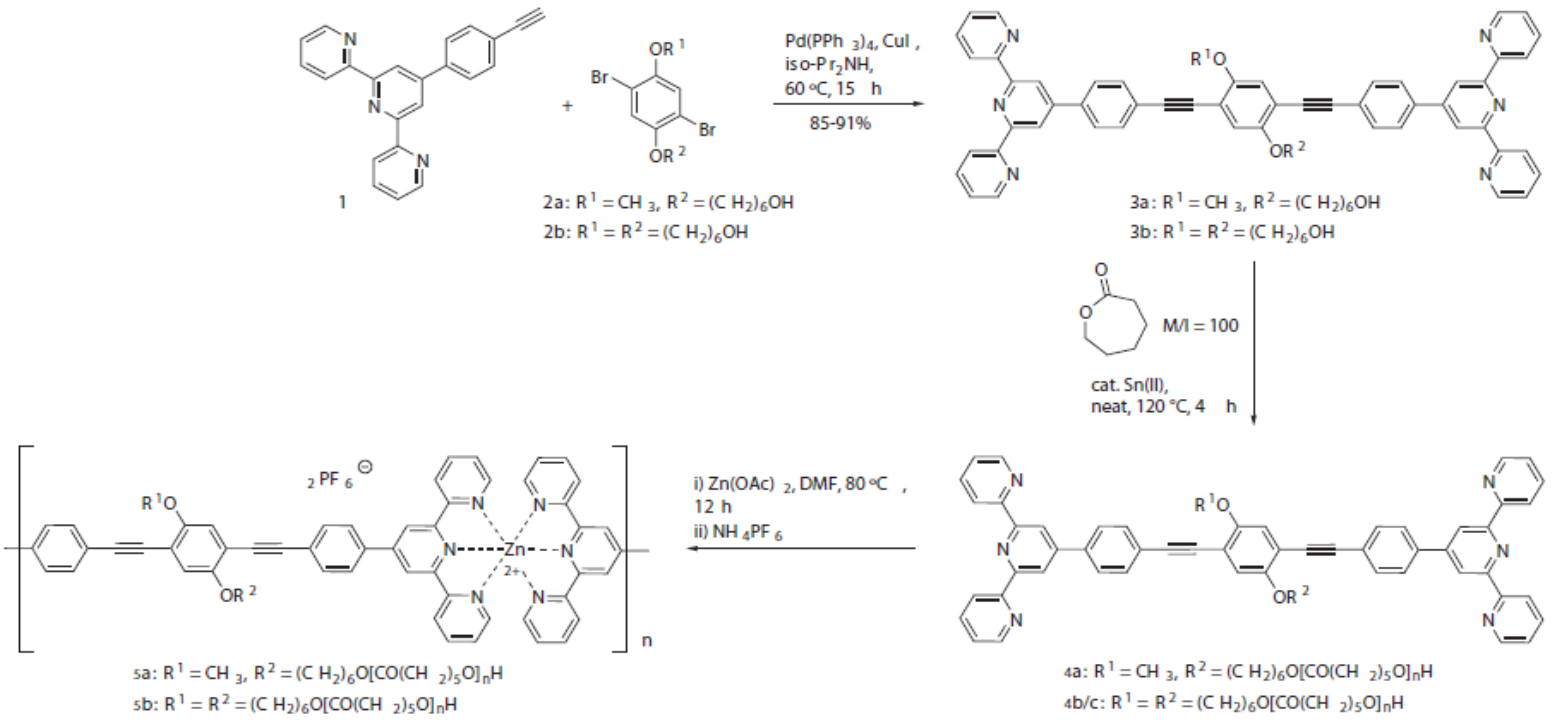
Introducing solubilizing groups increase solubility of metallopolymer-----



Macromolecules, **2006**, *39*, 8559–8566

Conjugated Metallopolymers with Terpyridines

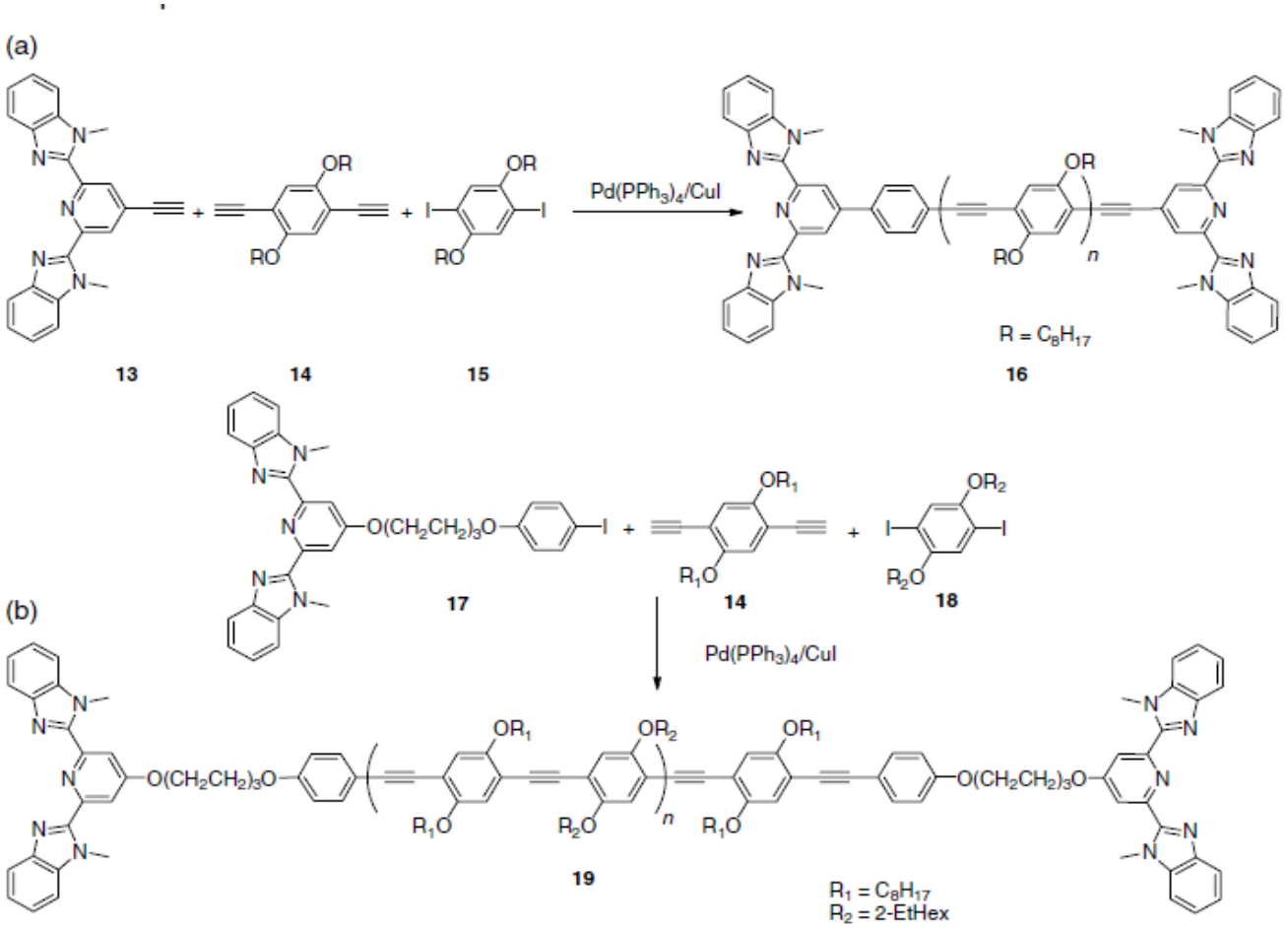
The Sonogashira reaction



Schubert, U. S. *et al.* Macromol. Rapid Commun. **2008**, *29*, 1679–1686

Terpyridines-like Conjugated Metallopolymers

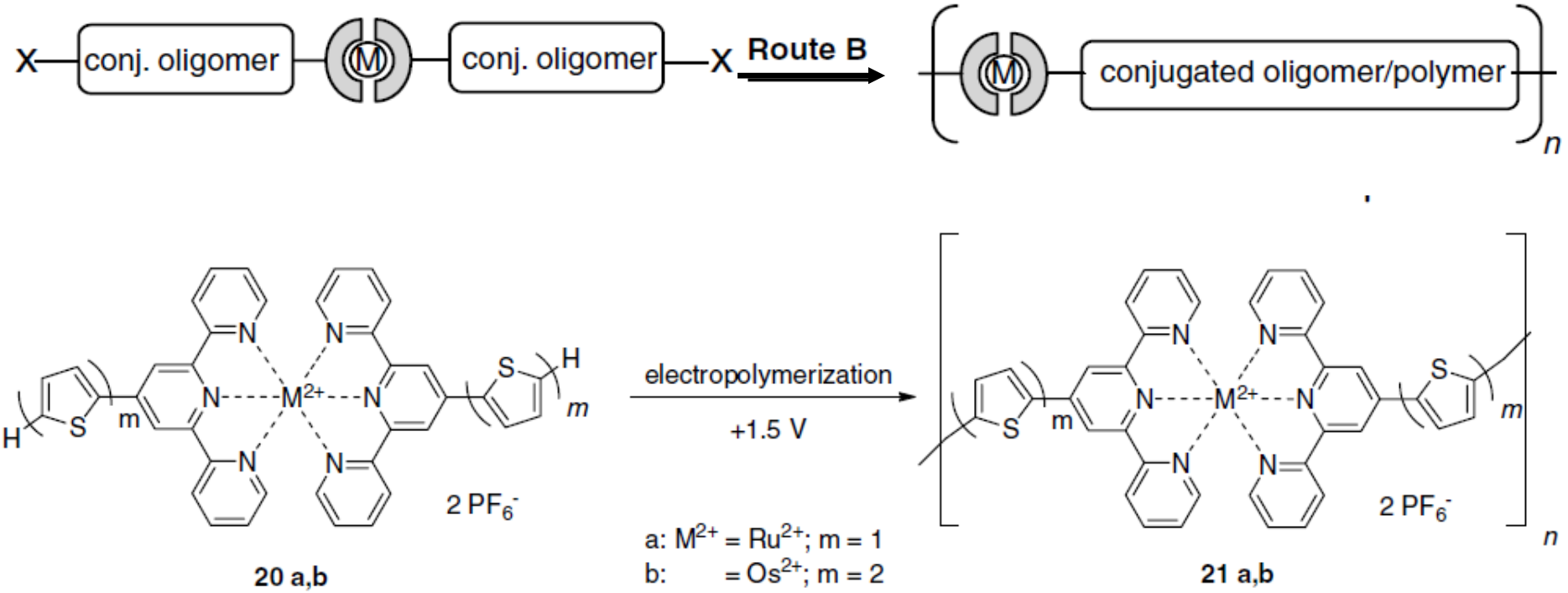
- **The synthesis of the conjugated macroligand and the decoupled macroligand**



Weder et al. Macromolecules **2006**, *39*, 651-657

Weder et al. Macromolecules **2008,** *41,* 2157-2163

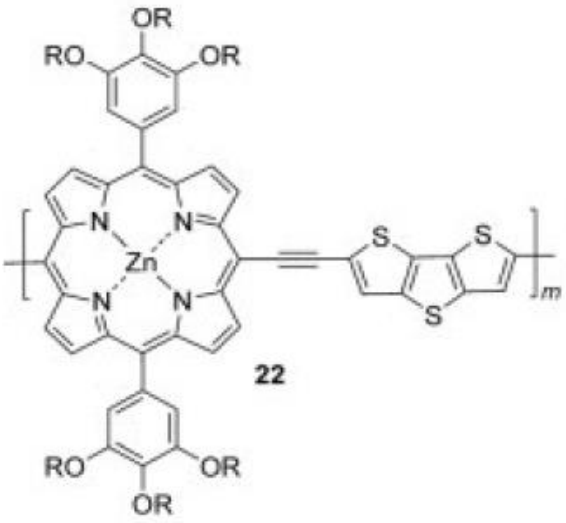
Conjugated Metallopolymers with Terpyridines



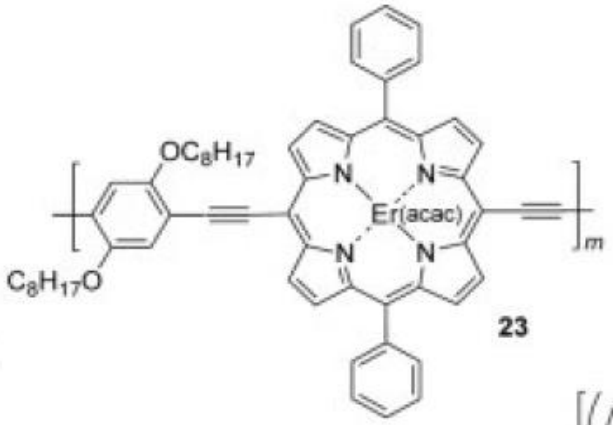
Robert J. Forster et al. *J. Phys. Chem. B,* **2003**, *107*, 10431-10439

π-Conjugated Polymers with Porphyrin Units as Part of the Main Chain

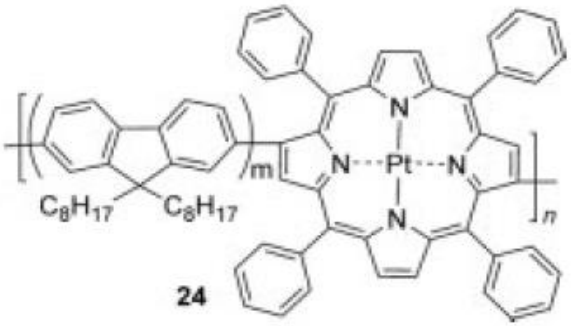
- **Several examples of conjugated polymers with porphyrin:**



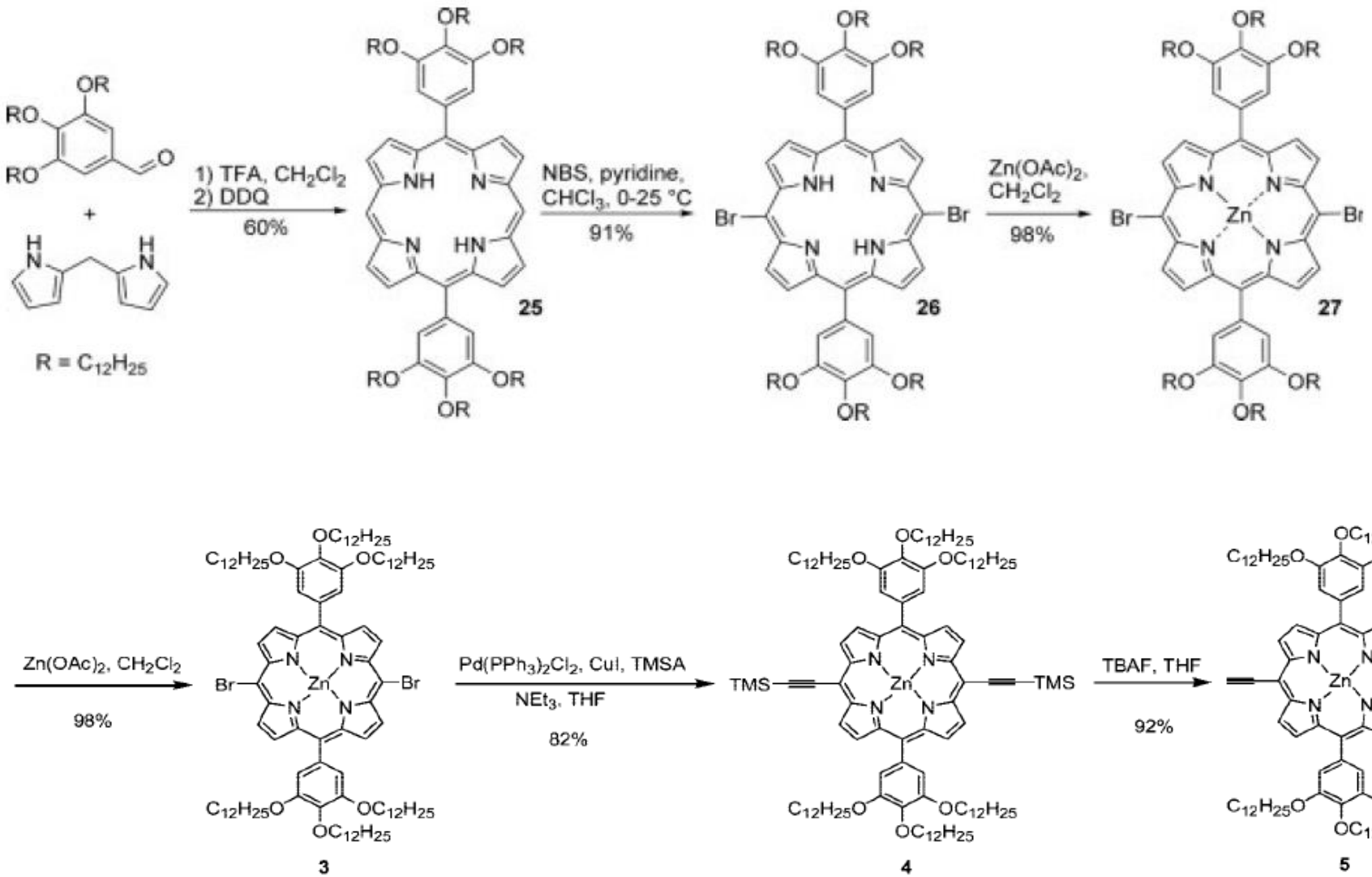
22



23

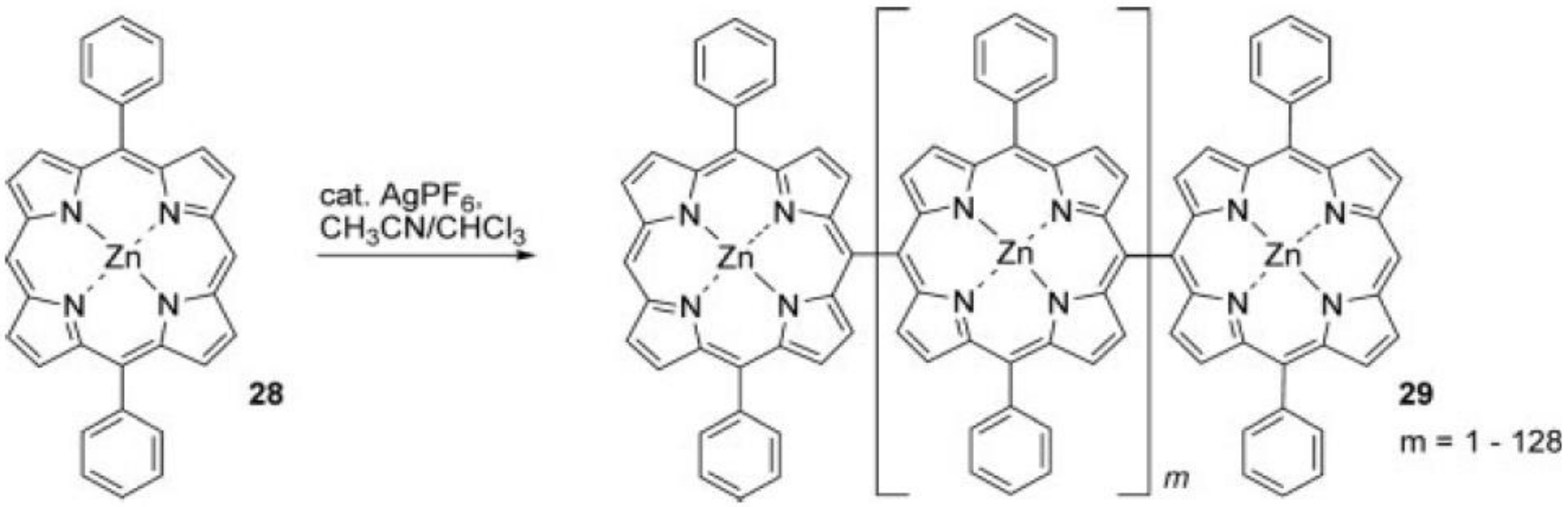


24



Macromolecules **2008**, *41*, 6895−6902

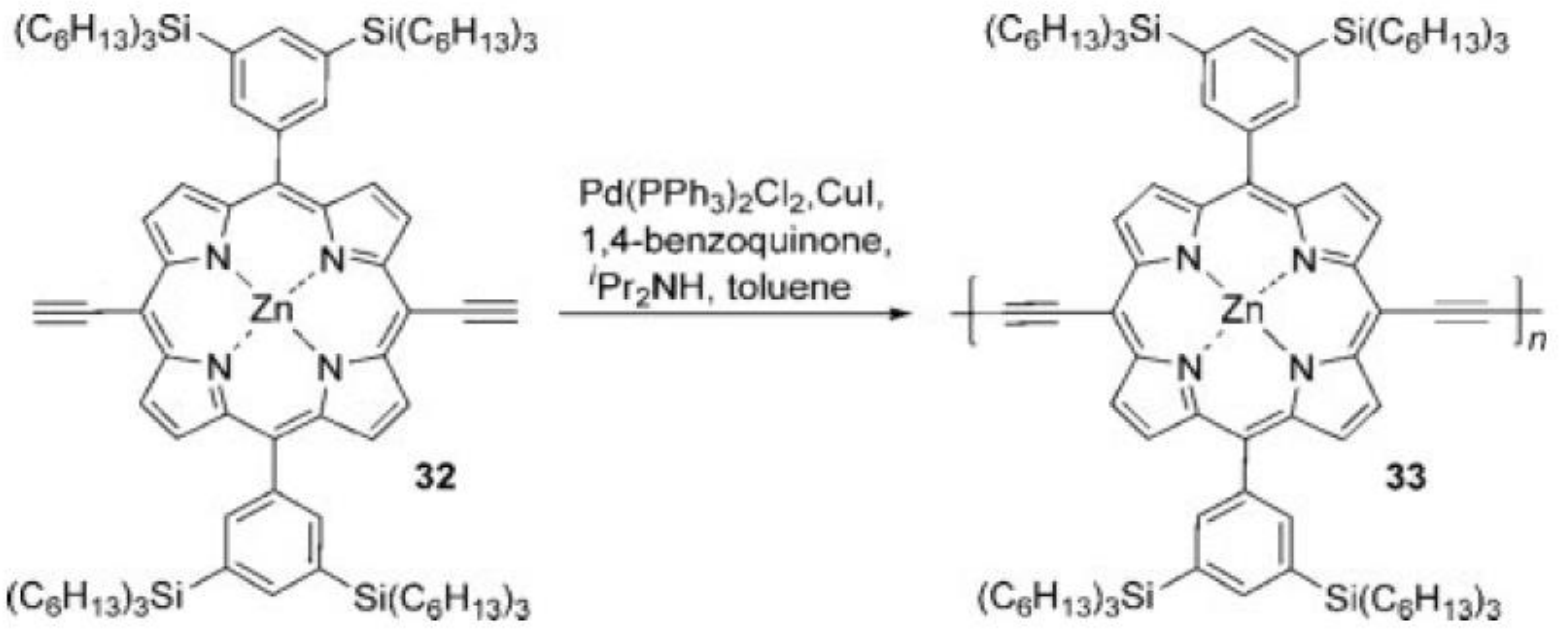
•**Homopolymerization of porphyrin derivatives**



DP up to 128, Mw up to 133 kg/mol by MALDI TOF MS

Aratani, N., Osuka, A., Kim, Y.H., Jeong, D.H., and Kim, D. *Angew. Chem. Int. Edit.*, **2000**, 39 (8),1458–1462.

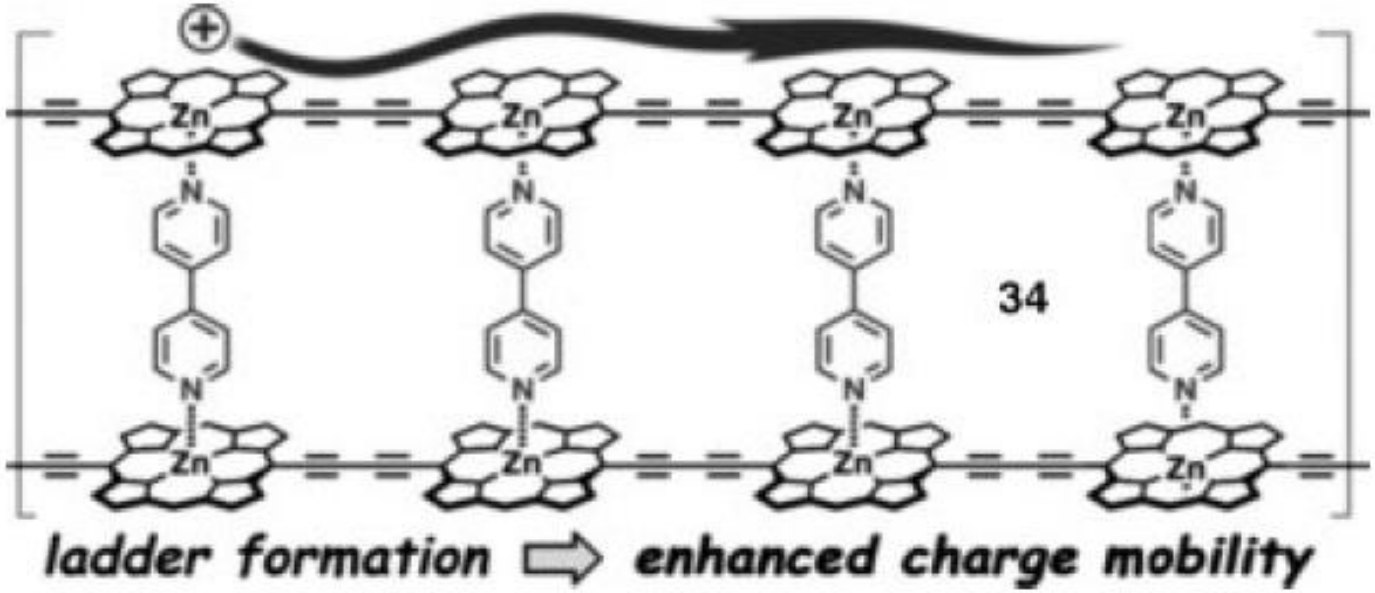
•**Straightforward (homo)polymerization a bisethynyl-functionalized porphyrin**



Mn: 83 700 da
DP: 50
PDI: 1.88

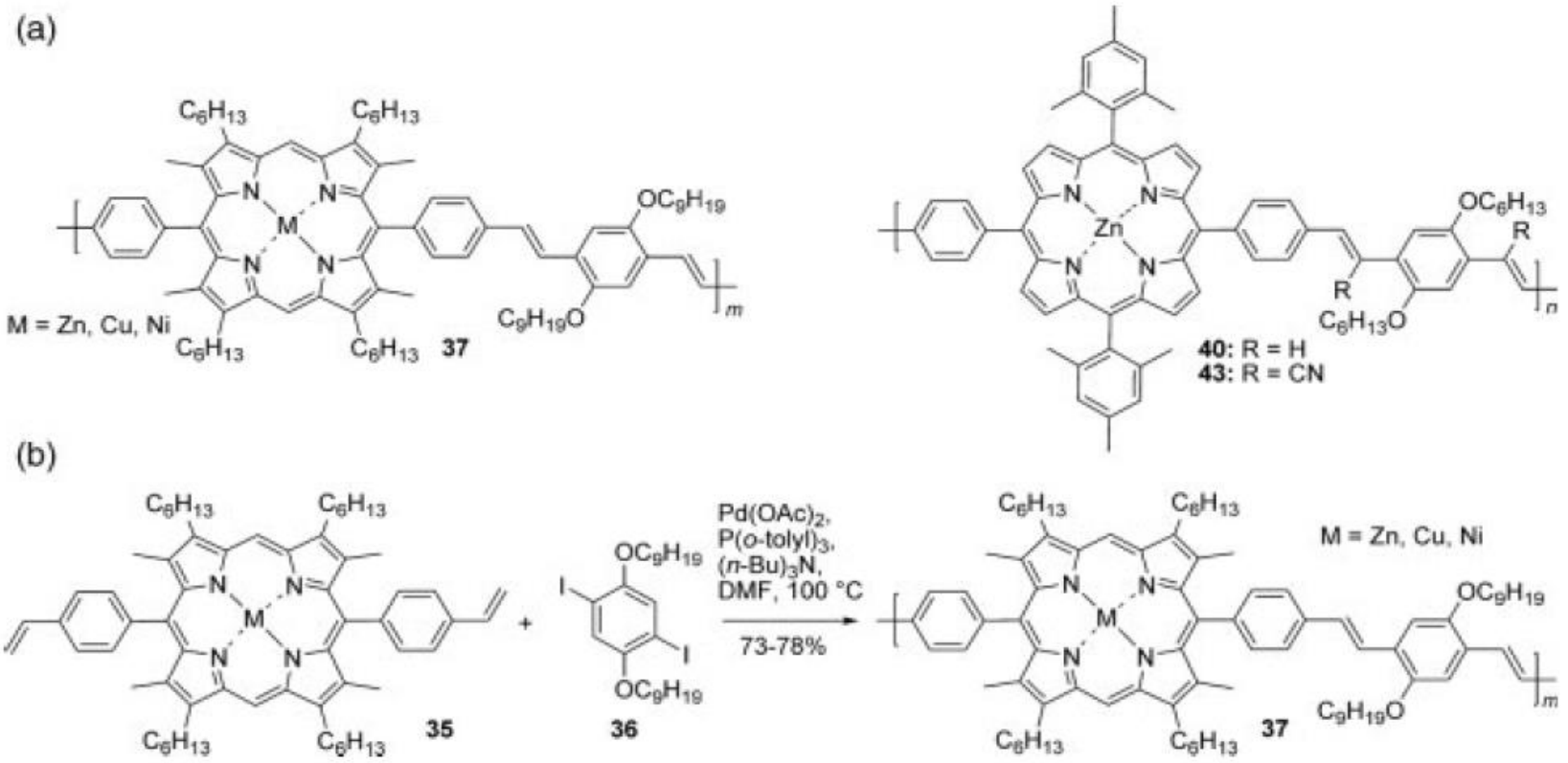
Anderson, H.L.et al. *J. Am. Chem. Soc.*, **2007**, *129* (44),13370–13371.

Double-strand ladder-type polyporphyrin



•**In these ladder-type structures the effective conjugation length could be increased remarkably, enhancing charge mobility.**

Anderson, H.L.et al. *J. Am. Chem. Soc.*, **2007**, *129* (44),13370–13371.

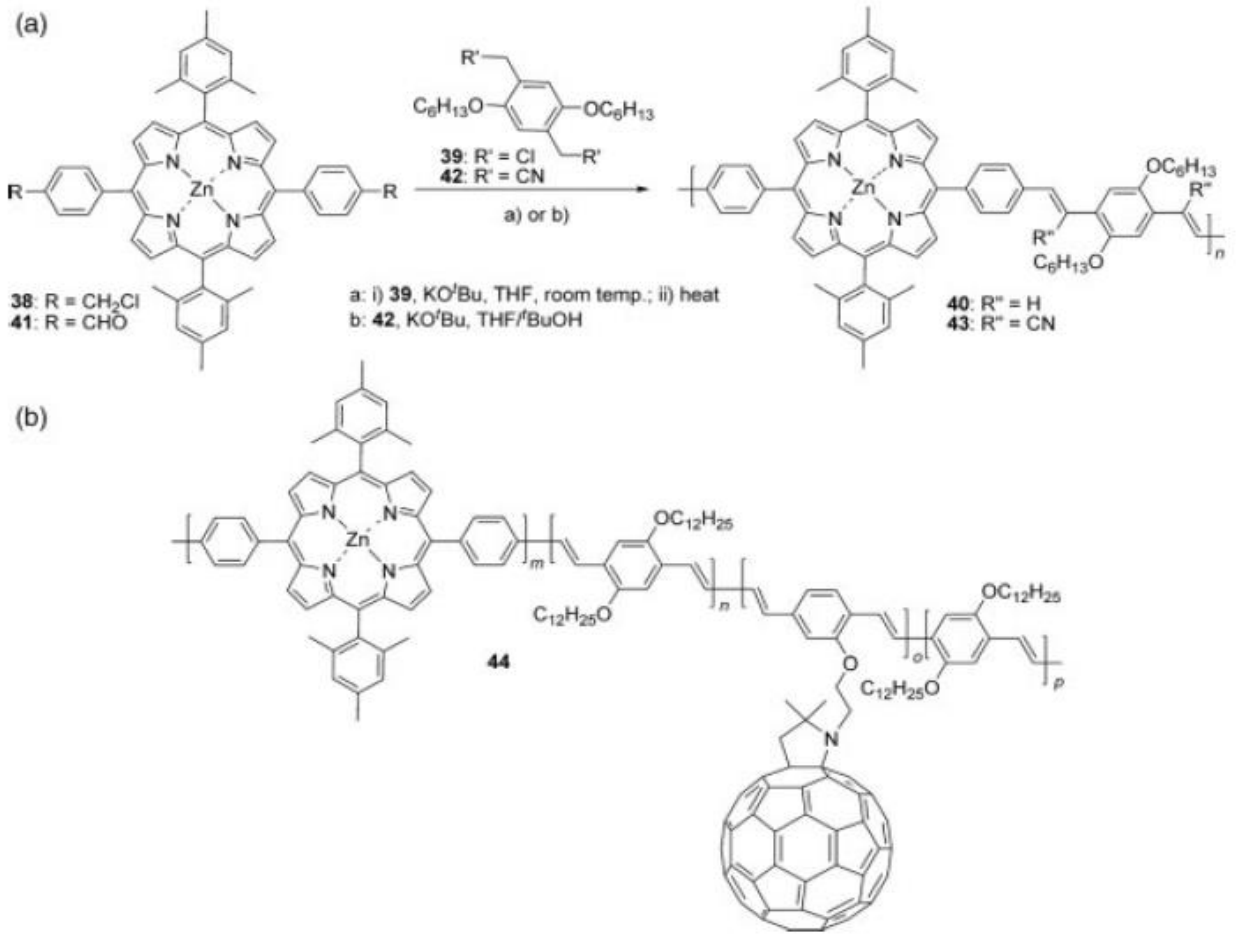


•Different types of conjugated porphyrin-pphenylenevinylene copolymers (a) and synthesis of the metalloporphyrin-containing PPV by Heck reaction (b)

•Under the reaction conditions utilized (i.e., DMF, 100 C) no exchange of the coordinated metal ions by the Pd(II)species could be observed

Bao, Z.N., Chen, Y.M., and Yu, L.P. *Macromolecules*,**1994**, *27*,4629–4631.

Two examples

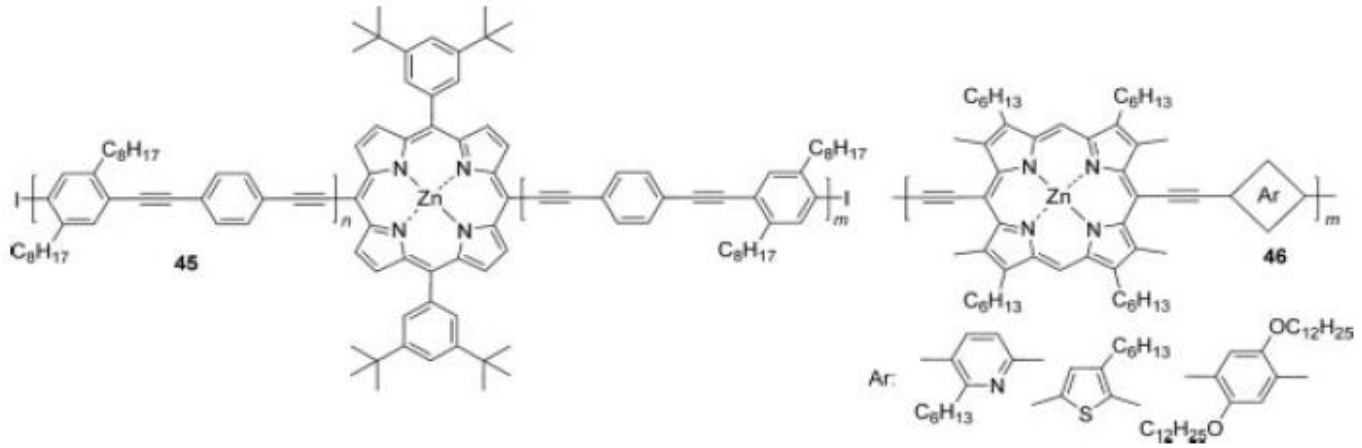


- **Heck reaction appears to be somehow superior to the conventional organic condensation reactions**
- **A promising candidate for photo induced electron-transfer systems**

Huang, C.S., Wang, N., Li, Y.L., Li, C.H.,Li, J.B., Liu, H.B., and Zhu, D.B. *Macromolecules*, **2006**, *39* (16) 5319–5325.

Conjugated Metallopolymers with Porphyrin

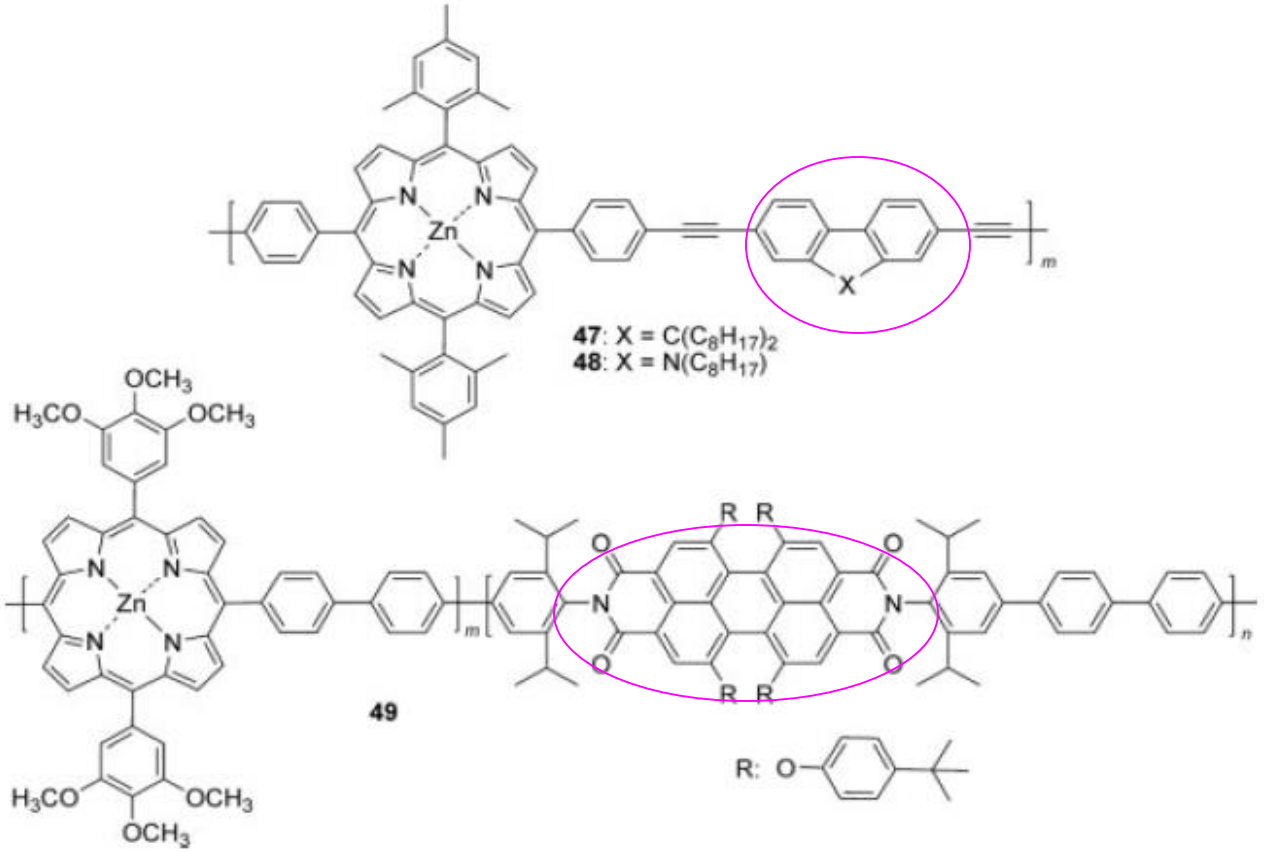
•**Two different types of metalloporphyrin-containing poly(p-henylenethylyne)s (PPEs) by Sonogashira cross-coupling reactions**



Nielsen, K.T., Spanggaard, H., and Krebs, F.C. Displays, **2004,***25* (5), 231–235.
Yamamoto, T., et al. *Macromolecules*, **2000**, *33* (16), 5988–5994

Conjugated Metallopolymers with Porphyrin

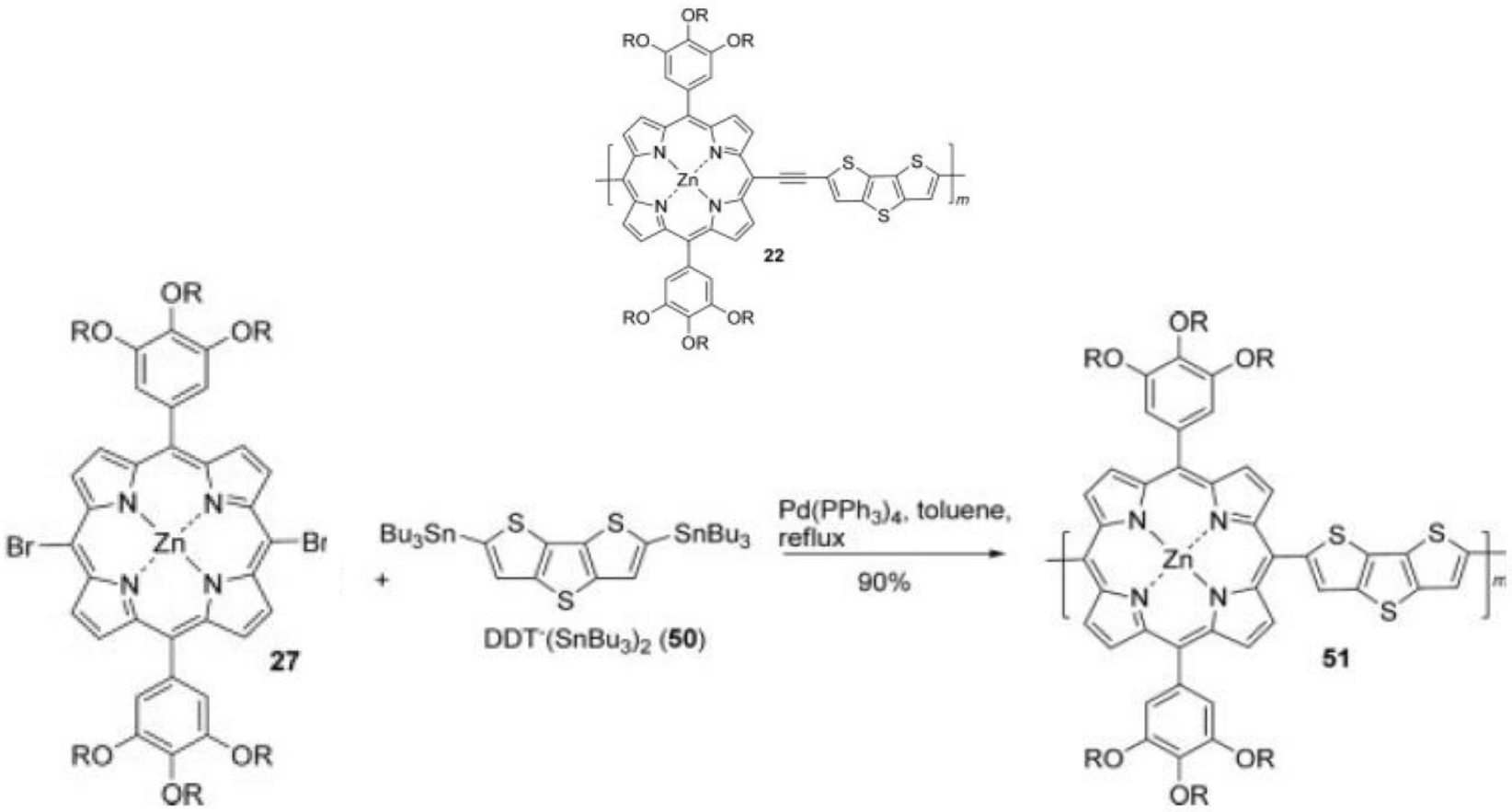
- **Connecting with chromophores**



Zhao, J.L., Li, B.S., and Bo, Z.S. *Chin. Sci. Bull.*, **2006**, 51, 1287–1295.

Zhu, D.B. et al. *J. Polym. Sci. Polym. Chem.*, **2006**, 44, 5863–5874.

Conjugated Metallopolymers with Porphyrin



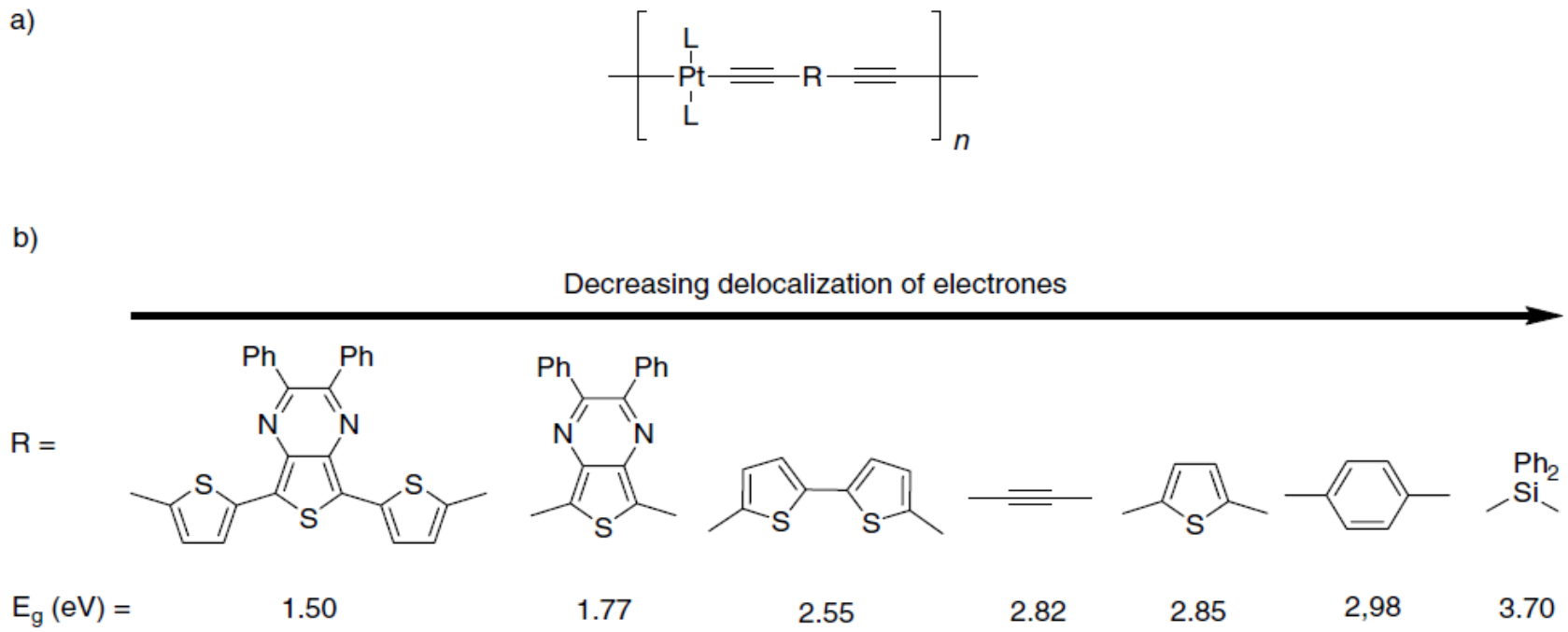
Mn: 46500 Da

Huang, X.B., Zhu, C.L., Zhang, S.M., Li, W.W., Guo, Y.L., Zhan, X.W., Liu, Y.Q., and Bo, Z.Z. (). Macromolecules, **2008**, *41* (19), 6895–6902.

Rigid-Rod Polymetallaynes

- Rigid-rod transition metal acetylide polymers represent a class of metallopolymers due to their unique structures and optoelectronic properties

Rigid-Rod Polymetallaynes

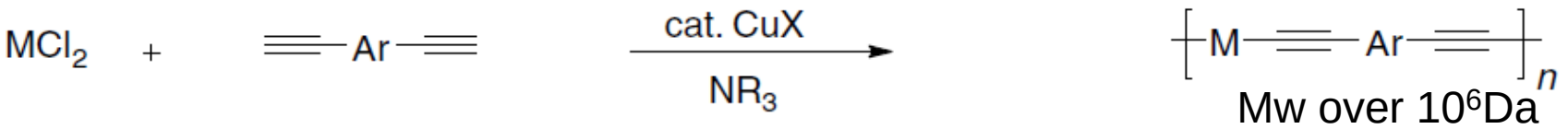


(a) Schematic representation of the general structure of a metal acetylide polymer; (b) trend in optical band gaps for platinum(II) polyynes with different spacer groups [170, 180].

Rigid-Rod Polymetallaynes

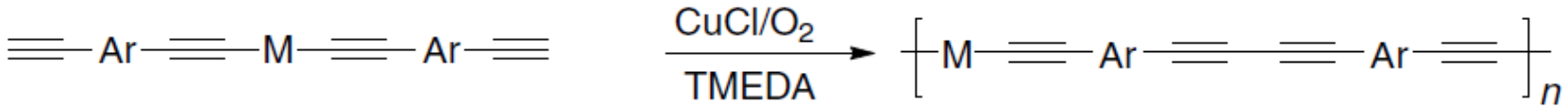
•Three synthetic routes for the synthesis of d^{10} metal alkynyl polymers.

a) Dehydrohalogenation

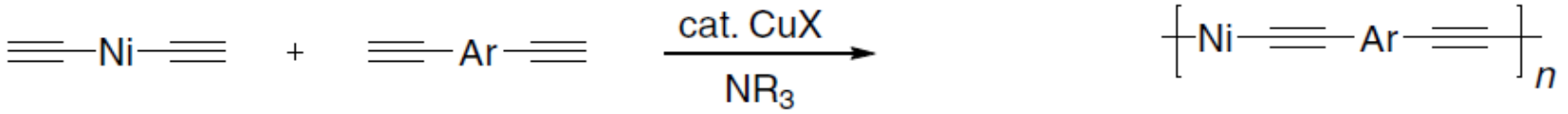


Mw over 10^6Da

b) Oxidative coupling



c) Alkynyl ligand exchange

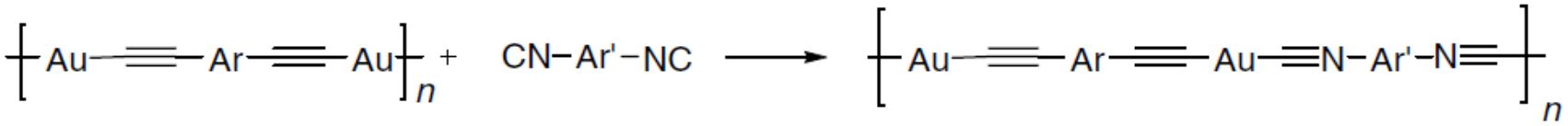


M = *trans*-Pt(PR_3)$_2$, *trans*-Pd(PR_3)$_2$
Ni = *trans*-Ni(PR_3)$_2$
Ar = none or aromatic spacer

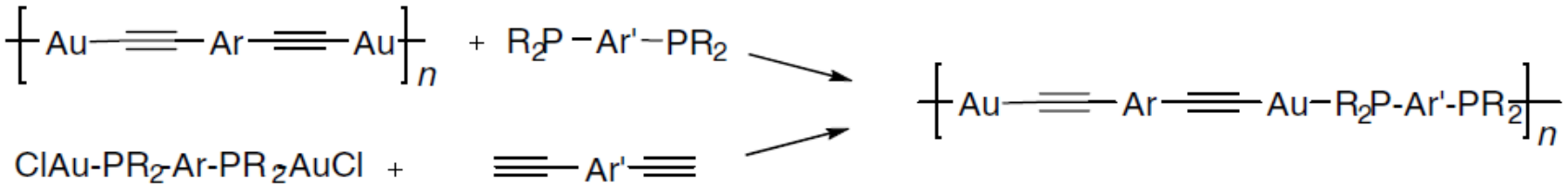
Rigid-Rod Polymetallaynes

- **Gold(I)-acetylides**

a)



b) Diphosphinoarene bridge

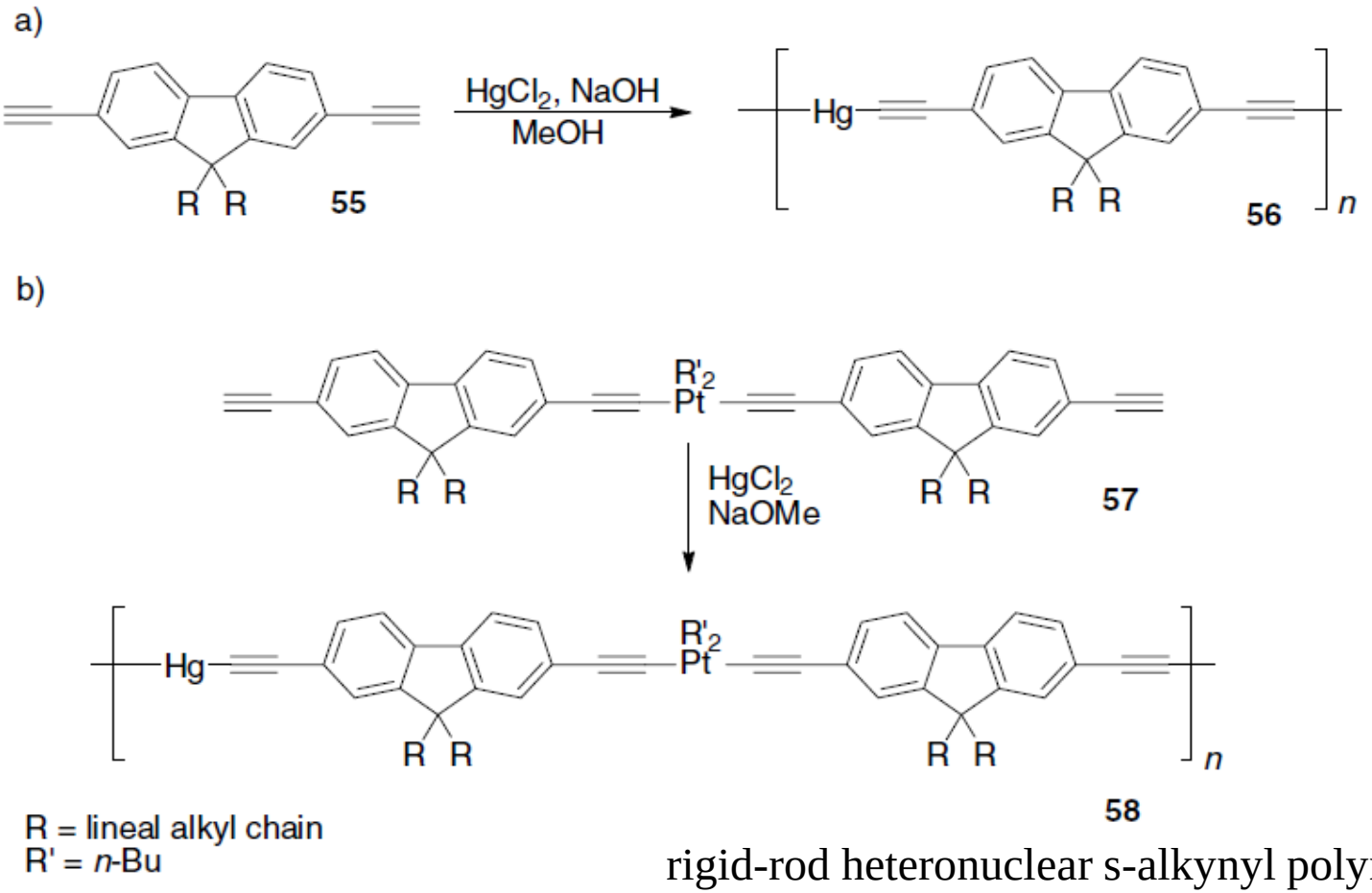


Ar, Ar' = aromatic spacer
R = phenyl or *i*-Pr

Jia, G.C., Puddephatt, R.J., Scott, J.D., Vittal, J.J.*Organometallics*, **1993,** 12 (9), 3565–3574.

Rigid-Rod Polymetallaynes

- **Mercury polyyne polymers**



rigid-rod heteronuclear s-alkynyl polymer

Wong, W.Y., Liu, L., and Shi, J.X. Angew. Chem. Int. Ed., **2003,** *42*, 4064–4068.

Zhou, G.J.,Wong,W.Y., Lin, Z.Y., and Ye, C. *Angew. Chem. Int. Ed*., **2006**, *45*, 6189–6193

Zhou, G.J., Wong, W.Y., Ye, C., and Lin, Z.Y. *Adv. Func. Mater*., **2007**, *17*, 963–975

Conclusion

•All synthetic routes for metallopolymers are uncontrolled polymerizations. The stoichiometry as well as the concentration is very important for the polymerization reaction. Therefore, the reproducibility of polymerizations is often a problem. However, the resulting polymers feature interesting properties can be used for emerging applications.

Thanks for your attention!