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Synthesis of Highly Insulated Molecular Wires by Polymerization of Organic-Soluble Symmetrical Linked Inclusion Complex Monomers

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Summary: We developed a new method for synthesizing an organic-soluble permethylated cyclodextrin-based insulated molecular wire (IMW); this method involves the polymerization of a symmetrical linked inclusion complex as a monomer. This monomer was synthesized by dimerization of linked inclusion complexes at the terminal alkynyl groups by Glaser coupling. The polyrotaxane thus obtained is highly soluble in a variety of organic solvents and has a high covering ratio, regioregularity, and photoluminescence efficiency.

Keywords: cyclodextrins; fluorescence; inclusion complexes; insulated molecular wires; rotaxanes

Introduction

π-Conjugated polymers are often described as molecular wires because of their high charge mobility. However, crosstalk and short circuits caused by internal π-π stacking interactions between these conjugated polymer chains can considerably deteriorate their electrical and optical behavior. Insulated molecular wires (IMWs) are particularly interesting because the core conjugated polymers are covered by a protective sheath, which limits the π-π interaction, thereby increasing the conductivity, fluorescence, solubility, and stability of these polymers as compared to those of the corresponding π-conjugated polymers.[1] Moreover, IMWs have attracted considerable attention because of their potential applicability as next-generation monomolecular electronic devices.[2] In the context of commercial availability and the efficacy of inclusion through hydrophilic-hydrophobic interaction of cyclodextrin (CD), methods for threading organic molecules through CDs have been researched extensively.[3] One of the methods for the synthesis of IMWs using CDs involves the threading of π-conjugated polymers through CDs[4] using the method developed by Harada et al. for the synthesis of a molecular necklace.[5] Another method involves the polymerization of pseudorotaxane formed by the inclusion of a conjugated monomer with a CD[6] or the copolymerization of pseudorotaxane, formed in the same manner, with linker molecules.[7] These polymers are soluble in water but generally insoluble in organic solvents; [8] this is because conjugated chains are covered with hydrophilic CDs. In addition, there exist partially uncovered sites and a considerable amount of residual water molecules, which is a disadvantage with respect to both the processing of the IMWs and their electrical properties. This reduces the potential of IMWs as an electronic material. Therefore, we decided to use permethylated cyclodextrin (PM CD) instead of native CD. The permethy-

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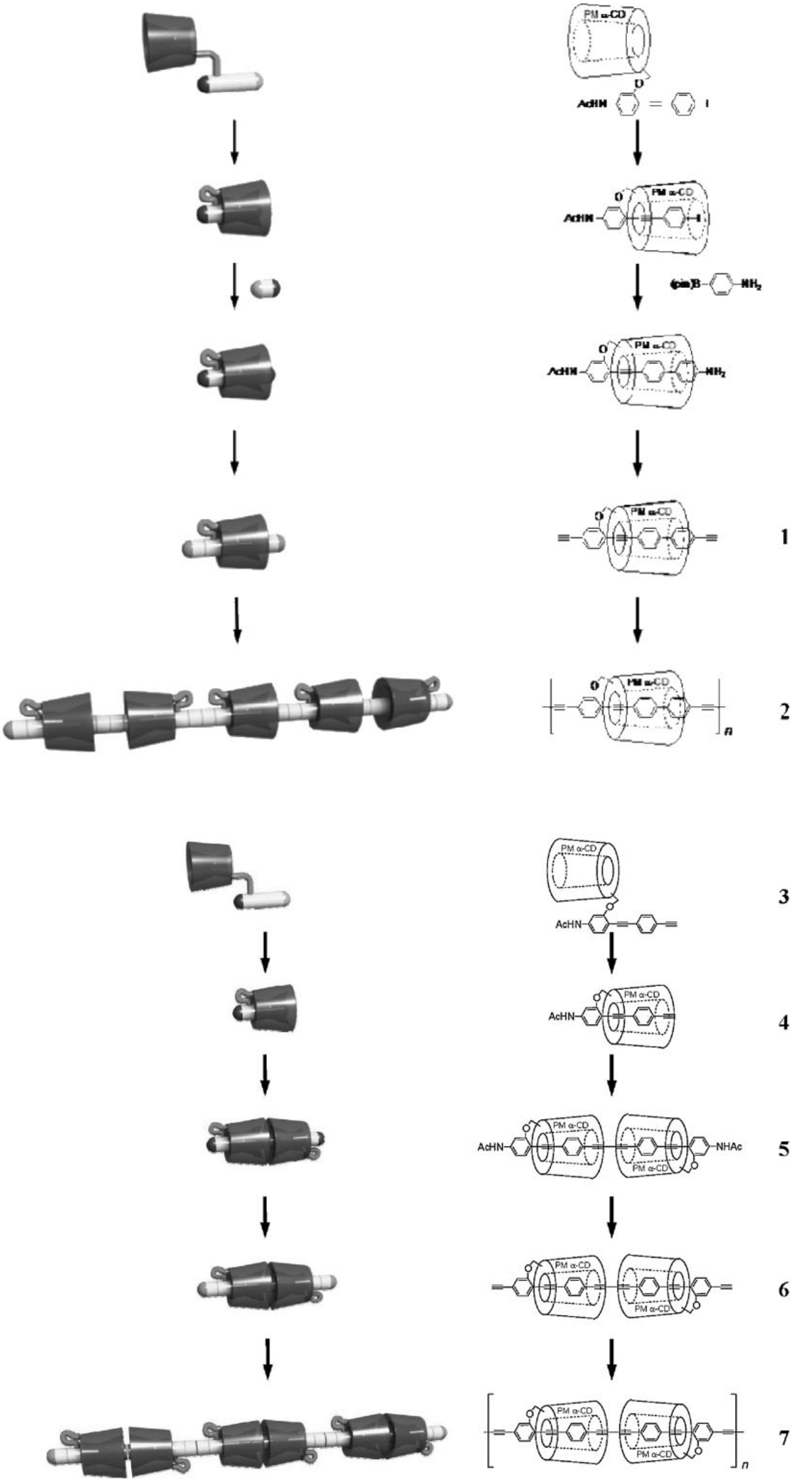
lation of all the hydroxyl groups of CD produces PM-CD, which has a deeper vacancy and higher solubility in organic solvents as compared to native CD. However, PM CD is insoluble in water, which is a disadvantage with regard to the formation of inclusion complexes by inclusion. In order to overcome this problem, we have prepared a guest-branched PM CD that can undergo intramolecular self-inclusion to form an inclusion complex.[9] During the course of this research, we developed a new method for synthesizing IMWs; this method involves the polymerization of PM CD-based inclusion complex monomers.[10] Our previous synthetic route to IMW is shown in Scheme 1 (Route 1). The intramolecular self-inclusion of the π-conjugated guest-branched PM CD forms an intramolecular inclusion complex, which is capped with a stopper molecule to afford a linked inclusion complex ([1]rotaxane).[11] Polymerization sites are introduced at both ends of this inclusion complex to form the corresponding monomer (**1**); this, in turn, is polymerized to afford a π-conjugated IMW (**2**) having random direction of CDs (head-head, head-tail, or tail-tail direction of the upper rim of adjacent CDs). In this study, we used this method to synthesize a structurally defined IMW by polymerization of a symmetrical linked inclusion complex (**6**, tail-tail type) as a monomer in order to add regioregularity and to increase the covering ratio of PM CDs against π-conjugated polymer chains (Scheme 1, Route 2).

Experimental Part

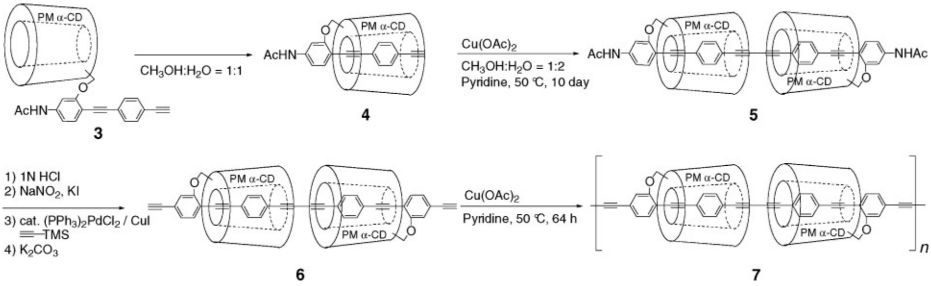
Synthesis

A symmetrical linked inclusion complex (**5**) was synthesized by a method previously reported by us, as shown in Scheme 2.[9b] The reaction of 6-*O*-monotosyl PM α-CD with 2-iodo-5-acetamidophenol resulted in a modified PM α-CD iodide in 98% yield. Sonogashira coupling of this iodide with (4-ethynylphenylethynyl)trimethylsilane followed by deprotection of the trimethylsilyl group gave an ethynyltolan-linked PM α-CD (**3**) in 71% yield. The intramolecular self-inclusion of **3** has been confirmed by solvent- and concentration-dependent ^{1}H NMR methods. Next, we carried out dimerization of the linked inclusion complex **4** by using Glaser coupling in H_2O/CH_3OH/pyridine (10/5/1) at 50 °C for 10 days. The formation of the desired symmetrical linked inclusion complex (**5**) was inferred from the MALDI-TOF mass spectrum and NMR analysis. We then derived alkynyl groups from both acetamide groups of **5**. Deprotection of the acetamide groups of **5** yielded diamine; the diamine was treated with $NaNO_2$ and KI to afford the corresponding symmetrical linked inclusion complex diiodide in 66% yield. Finally, Sonogashira coupling of this diiodide with trimethylsilyl acetylene followed by deprotection of the trimethylsilyl group yielded **6** having two terminal ethynyl groups at both ends of the π-conjugated unit in 37% yield in four steps. As shown in Figure 1, the structure of **6** was characterized by 2D ROESY NMR; this is because there are NOEs between the protons in the tolan moiety and the H_3 and H_5 protons in the interior of the PM CDs. It is particularly worth noting that both PM α-CDs act as stopper groups to fix the inclusion complex structure. Studies performed using space-filling models, as shown in Figure 2, revealed that the covering ratio of PM α-CDs in the π-conjugated backbone of **6** was approximately 77%, which was much larger than that of the [1]rotaxane monomer **1** (60%). Thus, we carried out Glaser polymerization of monomer **6** (3.5 mM) in the presence of $Cu(OAc)_2$ (50 mM) in pyridine at room temperature.

According to GPC analysis, as shown in Figure 3, the monomer **6** completely disappeared after 64 h and the formation of regioregular IMW **7** was confirmed. As shown in Figure 4, the peaks in the ^{1}H NMR spectrum of **7** were broader than those in the NMR spectrum of **6**, indicating that the inclusion complex structure was maintained during polymerization. The M_n, M_w, and PDI of **7** were estimated to be 1.55×10^4,



Scheme 1.
Synthetic routes to PM CD-based IMWs **2** (rote 1) and **7** (route 2).



Scheme 2.
Synthesis of regioregular IMW **7** by polymerization of symmetrical linked inclusion complex **6** as the monomer.

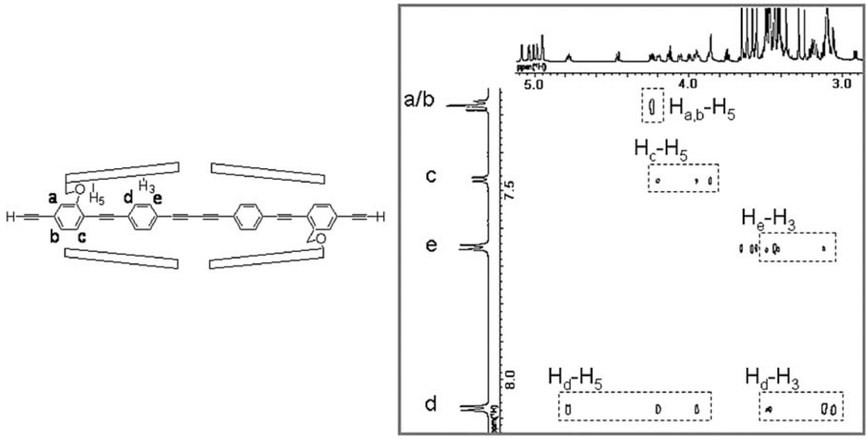


Figure 1.
400 MHz ROESY NMR spectrum of a symmetrical linked inclusion complex **6** in $CDCl_3$ at 25 °C.

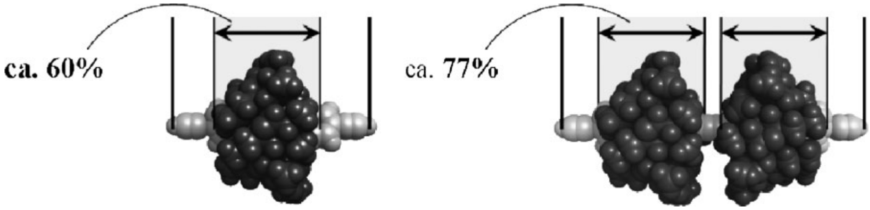


Figure 2.
Space-filling model of linked inclusion complexes **1** and **6**.

9.74×10^4, and 6.28, respectively, by using polystyrene as the calibration standard in the analysis.

The MALDI-TOF mass spectrum of **7** provides excellent evidence of its structural authenticity (Figure 5). All the observed peaks correspond to the expected singly charged molecular ions.

Results and Discussion

Solubility

IMW **7** thus obtained was soluble in various organic solvents such as ethyl acetate (26 mg/mL), chloroform (34 mg/mL), toluene (3 mg/mL), and dimethylformamide (52 mg/mL); this is because the

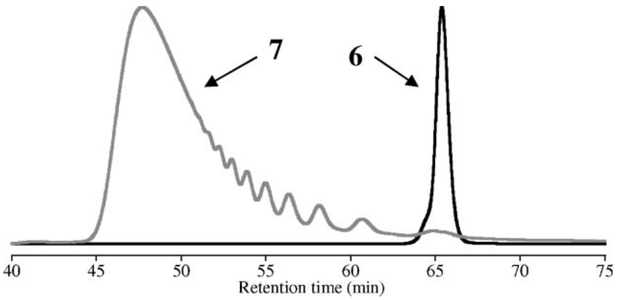


Figure 3.
GPC analysis of monomer **6** and IMW **7**.

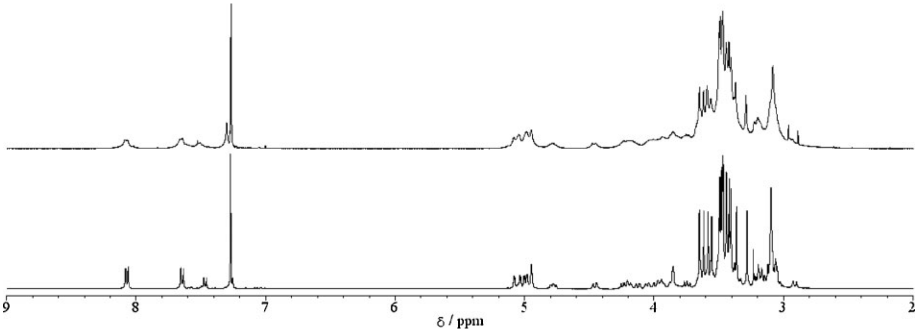


Figure 4.
(a) ^{1}H NMR (400 MHz, $CDCl_3$) spectra of monomer **6** (bottom) and IMW **7** (top).

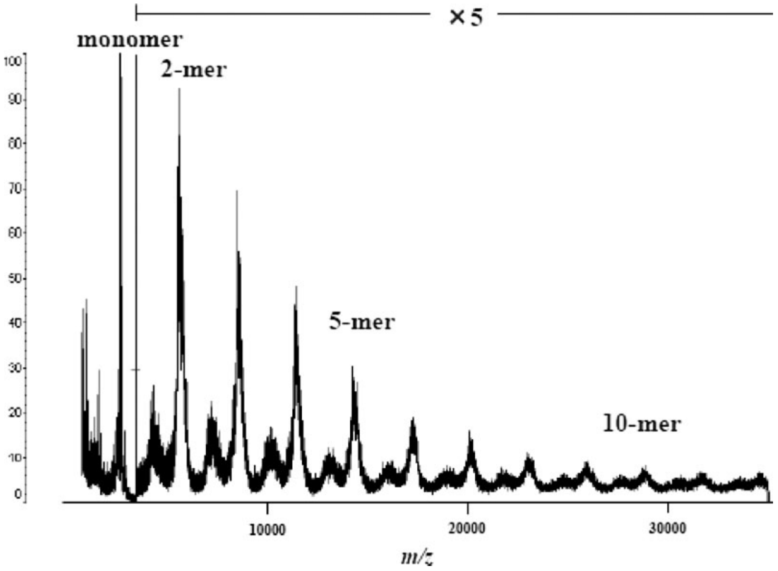


Figure 5.
MALDI-TOF mass spectrum of IMW **7**.

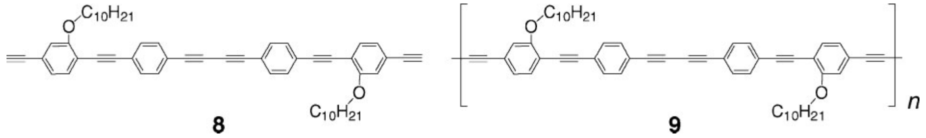


Figure 6.
Structures of the uninsulated monomer **8** and the corresponding polymer **9**.

Table 1.
Absorption and emission wavelength and fluorescence quantum yields of **6**–**9**.[a)]

Compound	Absorption (λ_{max}/nm)	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
6	357	397, 420	0.49	0.17
7[b)]	402	425, 450	0.52	0.14
8	368	403, 427	0.61	0.073
9	—	—	—	<0.002

[a)] The spectra were recorded in THF. The absolute quantum yields were determined by a calibrated integrating-sphere system.[b)] The high molecular weight polymer **7** ($M_n = 2.38 \times 10^5$, $M_w = 2.82 \times 10^5$, and PDI $= 1.2$) was separated by GPC.

π-conjugated chain is coated with highly organic-soluble PM CDs.

Electronic Spectra

In order to examine the insulating effect of PM α-CDs, the uninsulated compound **8,** which has the same π-conjugated unit as **6** and the corresponding polymer **9** were synthesized as reference compounds (Figure 6). Unfortunately, **9** was insoluble in all organic solvents because of the strong π-π interaction between the π-conjugated polymer chains. The absorption and emission wavelength of **6**, **7**, and **8** in the solution are shown in Table 1. The elongation of the π-conjugated backbone from monomer **6** to the IMW **7** resulted in a red-shift by about 45 nm. According to the spectra obtained from **6** and **8**, slight blue-shifts are observed in both the absorption and the emission spectra of **6**. These shifts suggest that the structure of the π-conjugated guest was changed by insulation using PM CDs.

Fluorescence Quantum Yields

The photoluminescence quantum yields of **6**–**9** are summarized in Table 1. As expected, significant fluorescence enhancements are observed in **6** and **7** as compared to the corresponding uninsulated compounds **8** and **9**, particularly in the solid state; this indicates that encapsulation of π-conjugated units by PM α-CDs enhances the fluorescence properties of these π-conjugated units.

Conclusion

A highly organic soluble and highly insulated π-conjugated compound was synthesized by dimerization of linked inclusion complexes using Glaser coupling. This unique supramolecular structure was determined by 2D NMR measurements. We have also developed a new method for synthesizing a CD-based regioregular IMW by polymerization of structurally defined symmetrical linked inclusion complex monomers. The symmetrical linked inclusion complex and regioregular IMW thus obtained have a high covering ratio and PL efficiency. Further, they are readily soluble in a variety of organic solvents. The absolute quantum yield indicated that the present insulated compounds exhibit an insulation effect.

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