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Synthesis of Insulated Pt–Alkynyl Complex Polymer

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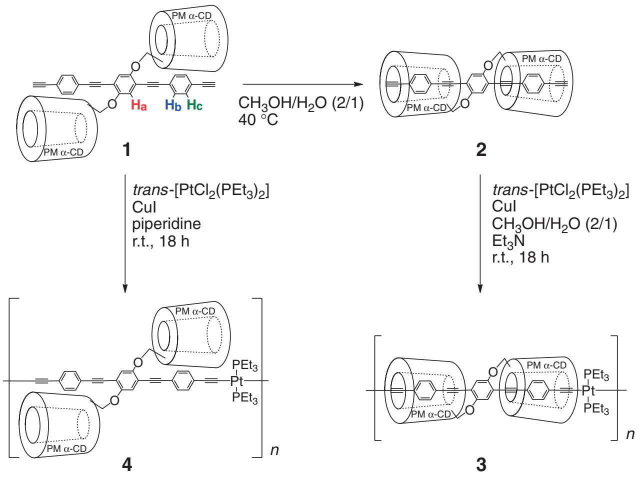
A Pt–alkynyl polymer in which the π-conjugated chain was completely covered with macrocycles was synthesized by intramolecular self-inclusion of an oligomeric phenyleneethynylene as a guest moiety with two permethylated α-cyclodextrins as hosts followed by copolymerization with a Pt(II) complex.

π-Conjugated polymers have attracted considerable attention in the search for light, low-cost, and flexible materials for electronic devices because of their high charge mobility and luminescence efficiency. In this context, insulated molecular wires (IMWs), in which the π-conjugated chains are covered with protective sheathes, have received particular attention due to their potential applicability as wiring materials in molecular electronics.[1] We recently developed a new method for synthesizing π-conjugated IMWs having polyrotaxane structures by polymerization of π-conjugated rotaxane monomers bearing permethylated α-cyclodextrins (PM α-CDs) as macrocycles.[2] Further, we confirmed that such IMWs were suitable materials for molecular electronics[3] because they had a high covering ratio, solubility in various organic solvents, rigidity, photoluminescence efficiency,[4] and charge mobility.[5] While these carbon-rich π-conjugated polymers are well-known, interest in π-conjugated polymers with metal centers in the polymer backbones has grown because of several unique properties (redox, magnetic, optical, and electronic properties) compared with conventional carbon-rich π-conjugated polymers.[6] Among such metal-containing polymers, metal–alkynyl polymers[7] which can be easily synthesized are very promising as next-generation functionalized molecular wires because of their nonlinear optical effects,[8] photoconductivity,[9] and electronic communication.[10] We have focused on the synthesis of insulated metal-containing π-conjugated polymer in which the metal element is introduced on the main chain. Herein we report the synthesis of an insulated Pt–alkynyl polymer by copolymerization of insulated π-conjugated monomers with *trans*-[$PtCl_2(PEt_3)_2$].

Scheme 1 shows the synthetic route to insulated Pt–alkynyl polymer **3**. The precursor of insulated π-conjugated monomer having two PM α-CDs on the center of an oligo(phenyleneethynylene) (OPE) unit **1** was prepared by our reported procedure.[4] The formation of insulated π-conjugated monomer **2** by sequential intramolecular self-inclusion of an OPE unit with two PM α-CDs was confirmed from the ^1H NMR spectrum recorded in a hydrophilic 2:1 $CD_3OD:D_2O$ solution (Figure 1b). The formation of **2** resulted in the following downfield shifts of aromatic protons as compared with ^1H NMR spectrum of **1** recorded in a lipophilic CD_2Cl_2 solution (Figure 1a): ($\Delta H_a = 0.36$ ppm, $\Delta H_b = 0.52$ ppm, and $\Delta H_c = 0.18$ ppm). These remarkably large downfield shifts suggest that the protons are located very close to the oxygen atoms of the methoxy groups or the α-1,4-glucosidic units of PM α-CD.[11] Under the same hydrophilic solvent condition as in the formation of **2**, the desired insulated Pt–alkynyl polymer **3** ($M_w = 3.1 \times 10^5$, $\tilde{n} = 97$, PDI $= 7.1$) was obtained by Cu-catalyzed copolymerization of thus formed monomer **2** with *trans*-[$PtCl_2(PEt_3)_2$] (1.0 equiv) in the presence of Et_3N under ambient temperature over a period of 18 h.[14] In order to examine the covering effects of PM α-CDs, the uninsulated polymer **4** ($M_w = 1.6 \times 10^5$, $\tilde{n} = 49$,



Scheme 1. Selective syntheses of the insulated polymer **3** and the corresponding uninsulated polymer **4** by changing solvents.

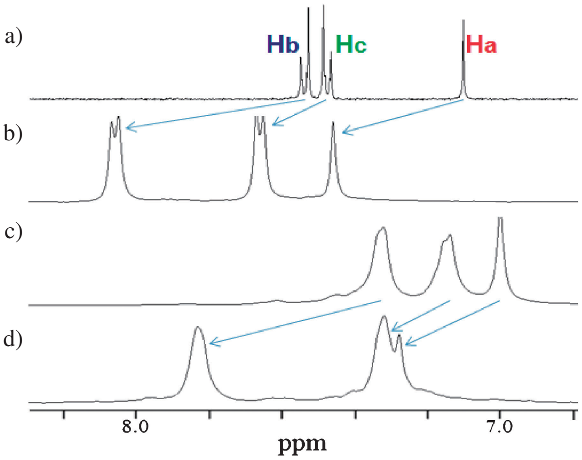


Figure 1. ^1H NMR spectra (400 MHz) in aromatic region of a) uninsulated monomer **1** in CD_2Cl_2, b) insulated monomer **2** in 2:1 $CD_3OD:D_2O$, c) uninsulated polymer **4** in CD_2Cl_2, and d) insulated polymer **3** in CD_2Cl_2.

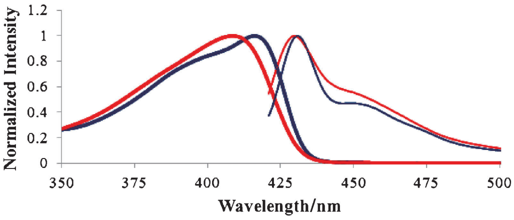


Figure 2. UV–vis absorbance (bold) and fluorescence (thin) spectra of **3** (red) and **4** (blue) in CHCl$_3$.

PDI = 3.6) was selectively synthesized as a reference via copolymerization of **1** with *trans*-[PtCl$_2$(PEt$_3$)$_2$] in a lipophilic solution (piperidine) instead of a hydrophilic solution (2:1 CH$_3$OH:H$_2$O).

As shown in Figures 1c and 1d, the peaks of OPE protons in the ^{1}H NMR spectrum of insulated polymer **3** also exhibit downfield shifts ($\Delta H_a = 0.28$ ppm, $\Delta H_b = 0.51$ ppm, and $\Delta H_c = 0.18$ ppm) as compared with those of uninsulated polymer **4**, which are similar to the shifts in the ^{1}H NMR spectrum of **2**. The peaks of PEt$_3$ protons in the ^{1}H NMR spectrum of **3** in CD$_2$Cl$_2$ exhibit upfield shifts ($\Delta H = 0.12$–0.16 ppm) as compared with those of **4** probably because the protons are located very close to the methyl groups of outer-ring lip of PM α-CD. They indicate that the insulated and uninsulated monomer structures were maintained during copolymerization and that selective synthesis of the insulated and uninsulated Pt–alkynyl polymers was achieved.

We confirmed the existence of Pt units in the polymer chain by the following spectroscopic analysis. The quantum yields of polymers **3** and **4** in CHCl$_3$ under atmospheric conditions were much lower (**3**: 0.5%, **4**: 0.4%) than those of carbon-rich IMWs that were synthesized from **2** via the Glaser coupling reaction, as described in our previous work.[4] This suggests that Pt was introduced into the π-conjugated polymer chain; fluorescence from OPE moieties should be quenched via $S_1 \rightarrow T_1$ intersystem crossing caused by the heavy-atom effect. Furthermore, the ^{31}P NMR spectra of **3** (12.15 ppm, $J_{\text{P–Pt}} = 2373$ Hz) and **4** (12.07 ppm, $J_{\text{P–Pt}} = 2355$ Hz) showed characteristic peaks with accompanying ^{195}Pt satellites, indicating that a *trans*-[Pt(PEt$_3$)$_2$] coordination geometry exists in the polymers.[12] Moreover, the integral ratio of the ^{1}H NMR spectrum of OPE units and ethyl groups of PEt$_3$ indicates that OPE and Pt units were introduced in almost a 1:1 ratio.

In order to examine the shielding effect of PM α-CD on the π-system, we compared the absorption spectra of **3** and **4** in CHCl$_3$ and DMSO (Figures 2 and 3). Comparison of the absorbance maximum of **3** (abs $\lambda_{\text{max}} = 408.5$ nm) with that of **4** (abs $\lambda_{\text{max}} = 416.0$ nm) in CHCl$_3$ shows that encapsulation of the OPE unit results in a blue shift of 7.5 nm due to shortening of the effective conjugation length of phenyleneethynylene units as a consequence of fixation in a twisted conformation by encapsulation (Figure 2).[13] Furthermore, while the absorbance maximum of **4** in DMSO solvent (abs $\lambda_{\text{max}} = 423.0$ nm) was red-shifted by 7.0 nm as compared with that in CHCl$_3$, the counterpart of **3** in DMSO (abs $\lambda_{\text{max}} = 407.0$ nm) showed little shift (Figure 3). This suggests that coordination of DMSO toward the OPE unit should decrease the LUMO level of excited uninsulated polymer **4**, causing a red shift in the absorbance maximum. This effect, however, was inhibited in insulated polymer **3** since OPE units are highly covered with PM α-CDs. Hence, it is clear that the insulation of OPE units dramatically led to inhibition of solvatochromism.

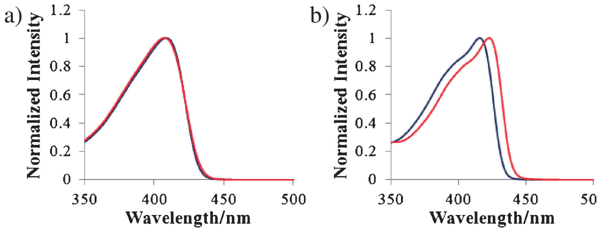


Figure 3. UV–vis absorbance spectra of a) **3** and b) **4** in CHCl$_3$ (blue) and DMSO (red).

In conclusion, we successfully synthesized insulated Pt–alkynyl polymer by intramolecular self-inclusion of an OPE monomer unit with PM α-CDs, followed by copolymerization with a Pt(II) dichloro complex. To our knowledge, this is the first example of the synthesis of an insulated Pt–alkynyl polymer with macrocycles. We also succeeded in selective synthesis of the corresponding uninsulated polymer by changing the solvent during copolymerization. The insulation effects are clearly reflected in the form of inhibition of solvatochromism. Experiments are in progress toward exploring the behavior of these new materials in molecular electronics.

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