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Synthesis of functionalized insulated molecular wires by polymerization of an insulated π-conjugated monomer**

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A new method for the synthesis of an insulated π-conjugated monomer was developed via the sequential self-inclusion followed by the elongation of the π-conjugated unit. The monomer was utilized in the synthesis of stimuli-responsive insulated molecular wires.

The field of molecular electronics is the most promising area for further innovation in information technology.1,2 In molecular electronics, each functionalized molecule has the potential to behave as a single device, such as a switch,3 socket,4 memory,5 light emitter,6 sensor,7 or transistor,8 which enables extensive integration and miniaturization. To realize such molecular electronics, various functionalized molecules must be wired between electrodes with nanosized gaps, in an efficient and dense fashion.3,9–12 Therefore, the development of techniques for the synthesis of definite-structure molecular wiring materials with appropriate functional groups and the development of an effective molecular wiring method is eagerly anticipated. In this context, our current research focuses on the synthesis of insulated molecular wires (IMWs)13–15 possessing high linearity, rigidity, stability, and high charge mobility.19–22 Herein, we report a new synthetic method for producing functionalized IMWs by polymerization of highly insulated oligo(phenylene ethynylene) (OPE) as a monomer.

The initial step of the current protocol was the design and synthesis of an insulated π-conjugated monomer based on the following considerations: (1) Permethyl α-cycloextrin (PM α–CD), used as a covering material, introduces high organic solubility; (2) π-conjugated OPE units provide the desired highly linear and rigid structure; and (3) the [3]rotaxane structure fixed by tether units is characterized by a high covering ratio and perfect structural regularity. We previously synthesized IMWs bearing poly(phenylene ethynylene) (PPE) units by the copolymerization of pseudo-linked [3]rotaxane 1 (Figure 1) with 1,4-diiodobenzene.20 In this method, a hydrophilic solvent system was required because the inclusion complex 1 was formed by hydrophilic-hydrophobic interactions. When we tried to prepare functionalized IMWs by the copolymerization of 1 with other functionalized π-conjugated diiodides instead of 1,4-diiodobenzene, we failed to obtain the desired products because of the steric hindrance issue and the insolubility of the diiodides in the hydrophilic medium. To overcome these problems, we tried to synthesize the insulated OPE 3 as a monomer having a fixed [3]rotaxane structure in the organic solvents. The synthetic route for generating the desired 3 is shown in Figure 1. Sequential self-inclusion of 1 in a hydrophilic solution (H2O/MeOH = 1/2) provided the pseudo-linked [3]rotaxane 1.20 A Sonogashira coupling reaction was used to fix the pseudo-linked [3]rotaxane structure by elongating the OPE unit: 1 was treated with tert-butyl(dimethyl)silyl (TBS)-protected p-iodophenylacetylene in the presence of catalytic amounts of Pd(OAc)2, tris(4,6-dimethyl-3-sulfanatophenyl)phosphine triosodium salt (TXPTS), and Cu. After deprotection of the TBS groups in 2 with tetr-n-butylammonium fluoride (TBAF), the desired insulated monomer 3 was obtained in high yield. The fixed [3]rotaxane structure was confirmed through analysis by 1H NMR analysis and ROESY NMR (see Supporting information, Figures SI1 and SI2).

Highly insulated OPE monomer 3 was soluble in various organic solvents and stable under reflux in toluene for 24 h without decomplexation, despite the lack of bulky stopper groups at the ends of the π-conjugated guest unit.

![Figure 1. Synthesis of insulated π-conjugated monomer.](image)

The synthesis of insulated poly(phenylene ethynylene) (PPE) was executed via Sonogashira copolymerization of 3 with 1,4-diiodobenzene in the presence of a catalytic amount of Pd(dba) and PPh3 in the organic medium (THF/Et3N = 2/1). The weight-average molecular weight ($M_w$) and polydispersity index...
(PDI) of the insulated PPE 4 were 1.21 × 10^3 and 3.21, respectively, determined by an absolute molecular weight determination technique using size–exclusion chromatography (SEC) with a low angle (7°) light–scattering detector. The average degree of polymerization (n) was found to be 40. Bithiophene, tetrafluorobenzene, or benzothiadiazole units could be introduced into the polymer backbone of the IMW using the corresponding dihalides as monomers, giving rise to 5, 6, and 7, respectively (Figure 2). The wavelengths of the absorption and emission maxima increased in the order 7 < 4 < 6 < 5, reflecting the extent of conjuagtion in the polymer backbones of these species (Figures S13a and S13b). This method was subsequently applied to the synthesis of stimuli–responsive IMWs by Sonogashira copolymerization of 3 with functionalized dihalides having a tetrathiafulvalene (TTF) unit as a redox group, a porphyrin unit as a metal–ion sensing group, and an azobenzene or diarylethene unit as a photoswitching group. These reactions gave rise to 8, 9a–c, 10, and 11, respectively (Figure 2).

Figure 2. Structures of functionalized insulated molecular wires.

The responses of these polymers to external stimuli were examined by first monitoring the change in the emission spectrum of functionalized IMW 8 bearing TTF moieties in response to redox manipulation, as shown in Figure 3. A seven–fold increase in the emission intensity of polymer 8 was observed in response to oxidation of the TTF moieties via the addition of the oxidizing reagent Fe(ClO4)3. Subsequent reduction of the oxidized TTF moieties with reducing agent FeCp2 returned the intensity to the initial level. This emission switching phenomenon can be attributed to photo–induced electron transfer (PET). Before oxidation and after reduction, an electron in each polymer should be transferred from the HOMO of the TTF moiety to the HOMO of the excited insulated OPE moiety via the PET mechanism, with consequent inhibition of the fluorescence emission. However, after oxidation, the fluorescence emission should be observed from the polymer because oxidation of the TTF moieties to the di–positive state lowers the HOMO levels and, therefore, inhibits PET (Figure S14a). Interestingly, however, no significant change in the emission intensity of the corresponding un–insulated polymer 8' was observed for the same redox reaction. The lack of emission switching in 8' was probably due to the higher HOMO level of the un–insulated OPE moiety relative to that of the insulated species, and thus, PET was ineffective regardless of the oxidation state of the TTF moieties (Figure S14b). Insulation constrains the conformation of the OPE chain in a somewhat twisted orientation, which prevents the delocalization of electrons along the conjugated chain and results in a decrease in the HOMO level (Figure S15).

Figure 3. a,b) Fluorescence spectra of polymer 8 and 8' in CHCl3 in different redox states: natural form (blue) and di–cation form (red).

Treatment of the zinc porphyrin IMW 9a with acid generated the corresponding non–metallated porphyrin IMW 9b. The difference in the charge mobilities of the metallated and non–metallated porphyrin IMWs was examined in the solid state by time–resolved microwave conductivity (TRMC) measurements (Figure 4a). In contrast to the conductivity transient observed for non–metallated porphyrin IMW 9b, zinc porphyrin IMW 9a exhibited a longer lifetime for the charged species on its backbone, with a clear signature of delayed charge carrier formation. This may have been due to the lowering of the SOMO with high symmetry (Figures S17a and S17b) by introduction of the metal center, as predicted by density functional theory (DFT) calculations. After zinc was re–introduced into the porphyrin center by treating 9b with Zn(OAc)2, the conductivity transient measured using TRMC led to a result that was identical to the result observed for 9a. On the other hand, iron porphyrin IMW 9c, formed by the treatment of 9b with FeCl2 and carbon monoxide, exhibited the highest photoconductivity transients, with extremely long lifetimes for the charged species (Figures 4a and S17c). Because of the remarkable potential of IMW 9c as a one–dimensional semiconductor material, its intramolecular charge carrier mobility was quantitatively assessed by combining TRMC and transient absorption spectroscopy (TAS) measurements (Figures 4b, 4c, and S17d). The partial overlap of the triplet absorption (570 and 750 nm) was considerable at 570 nm, and therefore, the charge carrier generation yield φ was overestimated to be 5 × 10−3 at 20 µs after pulse exposure, where the contribution from the triplet excited states to the conductivity transient was negligible. The shorter lifetime of the triplet excited states in the present case was due to triplet–triplet annihilation leading to free charge carriers on the backbone of 9c. In this case,
the rise time of the transient conductivity (Figure 4a) was identical
to that of the optical transients of the triplet excited states. The
intramolecular hole mobility values were estimated to be as high
as 0.1 cm²/(V s) (0.3 cm²/(V s) along the 9c backbone), which
indicated the existence of effective conductive pathways for
positive charges along the backbones of the iron–metallated
porphyrin moiety. These results also indicated that the porphyrin
IMWs switch both the stability and mobility of positive charges on
their backbones in response to variations of the coordinated metal
ion and to the absence or presence of a metal ion. Thus, it is
expected that this IMW could be applied to ion-sensing devices.
As shown in Figure 4d, a considerable enhancement in the transient
conductivity signal was observed for the zinc porphyrin IMW 9a
film annealed under oxygen atmosphere, reaching a value four
times that of the end-of-pulse conductivity. The saturated
film annealed under oxygen atmosphere, reaching a value four
times that of the end-of-pulse conductivity. The saturated
concentration of oxygen in the present case can be predicted to be
five-fold higher than that of the ambient (air-saturated)
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Figure 4. a) Conductivity transients observed upon excitation of cast films
of 9a (red), 9b (violet), and 9c (blue) at 355 nm using 1.9 × 10¹⁶ photons
⋅ cm⁻²; film thicknesses of 0.9–2.3 μm, and ambient conditions. b) Transient
absorption spectra of 9c at 1 (blue), 3 (violet), and 10 (red) μs after pulse
excitation at 355 nm (2.4 × 10¹⁶ photons cm⁻²). c) Kinetics traces for the
transient conductivity (blue) and optical absorption at 670 nm (violet) and
570 nm (red) in the 9c solid film. d) Conductivity transients observed upon
excitation at 355 nm at 1.8 × 10¹⁶ photons cm⁻² in a cast film of 9a under
ambient conditions (blue) and O₂ (red). The casted plate was placed in a
TRMC probe under O₂ at 70°C for 1 h and then cooled to room temperature
before transient conductivity measurement under O₂.

Conclusions

In summary, we designed and synthesized novel organic–soluble
insulated OPE monomers. Stimuli-responsive IMWs with
three different functions—redox switching, ion sensing, and
photoswitching—were successfully constructed using the novel
insulated OPE monomers.

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