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Synthesis of an insulated molecular wire by click polymerization†‡

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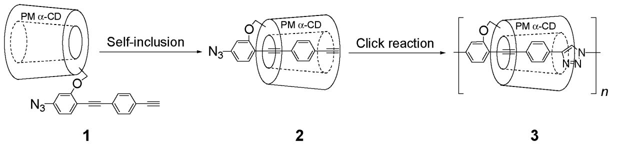
We developed a new method for the synthesis of an organic-soluble insulated molecular wire (IMW) with permethylated cyclodextrin (PMCD); this method involves click polymerization of linked [2]rotaxane containing azide and alkynyl groups at both ends of a π-conjugated guest.

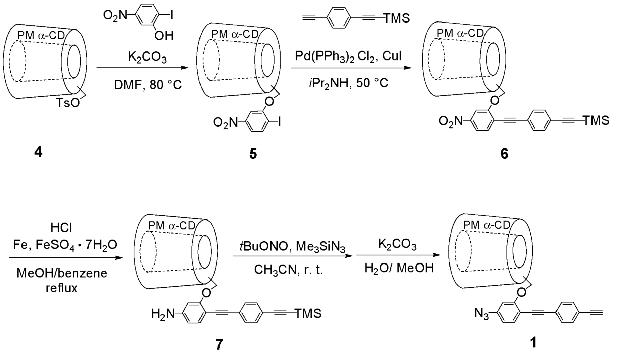
The copper(I)-catalysed azide–alkyne reaction, commonly referred to as a "click reaction", has a number of remarkable advantages: (1) high efficiency, (2) atom economy, and (3) high tolerance of functional groups. This reaction has attracted significant attention owing to its potential applicability in organic synthesis. Polymer chemists have also utilized this reaction to synthesize dendritic, hyper-branched, and linear macromolecules.[1,2] Although a few studies have been reported on the synthesis of π-conjugated polymers employing the click reaction,[3–6] to the best of our knowledge, there is no report on the synthesis of insulated molecular wires (IMWs) having a π-conjugated polymer chain as a backbone.[7] IMWs have generated considerable interest for next-generation monomolecular electronic devices.[8] Presently, we are interested in the synthesis of IMWs[9–12] having the following ideal features: (1) a π-conjugated polymer chain with a high degree of insulation, (2) a rigid polymer chain with high linearity, (3) high solubility in organic solvents, (4) high charge mobility, and (5) high regioregularity. We have recently developed a new method for the synthesis of an organic-soluble IMW by Glaser or Sonogashira polymerization of a lipophilic permethylated α-cyclodextrin (PMCD)-based linked [2]- or [3]rotaxane monomer formed by self-inclusion in hydrophilic solvents.[13–16] We intended to apply click chemistry to the synthesis of π-conjugated IMWs since the click reaction provides an aromatic 1,2,3-triazole skeleton and proceeds efficiently in hydrophilic solvents, which promotes the formation of a self-inclusion complex (PMCD-based rotaxane monomer) by a hydrophilic–hydrophobic interaction.[17–19] We disclose herein new methods for the synthesis of a defect-free PMCD-based IMW (**3**) *via* click polymerization of a self-inclusion complex (**2**) containing azide and alkynyl groups at the ends of the monomer (Scheme 1).



Scheme 1 Synthetic route to PMCD-based IMW *via* click polymerization.

π-Conjugated guest-linked PMCD (**1**) was synthesized from monotosyl PMCD (**4**)[20] *via* five steps, as shown in Scheme 2. Reaction of **4** with 2-iodo-5-nitrophenol resulted in an iodobenzene linked-PMCD (**5**) in 98% yield. Sonogashira coupling of **5** with (4-ethynylphenylethynyl)trimethylsilane and subsequent reduction of the nitro group gave an ethynyltolan-linked PMCD (**7**) isolated in 94% yield. **7** was then treated with *t*BuONO and Me_3SiN_3, which was followed by deprotection of the trimethylsilyl group to give **1** in 48% isolated yield *via* these two steps.

Intramolecular self-inclusion of π-conjugated guest-linked PMCD **1** was confirmed by a space-filling model and examined by ^1H NMR using different solvents and concentrations. As shown in Fig. 1, ^1H NMR analysis of **1** in $CDCl_3$ at room temperature revealed that the π-conjugated guest moiety was excluded from the cavity of the PMCD, whereas the spectrum in $(CD_3)_3COD$ at room temperature indicated the presence of a mixture of **1** and its inclusion complex (linked [2]rotaxane) **2**. When $D_2O:(CD_3)_3COD = 2:1$ was used as the solvent, **1** was completely converted to **2**. Formation of linked [2]rotaxane (**2**) resulted in the downfield shifts of aromatic protons in **2**, *i.e.*,



Scheme 2 Synthesis of π-conjugated guest-linked PMCD (**1**).

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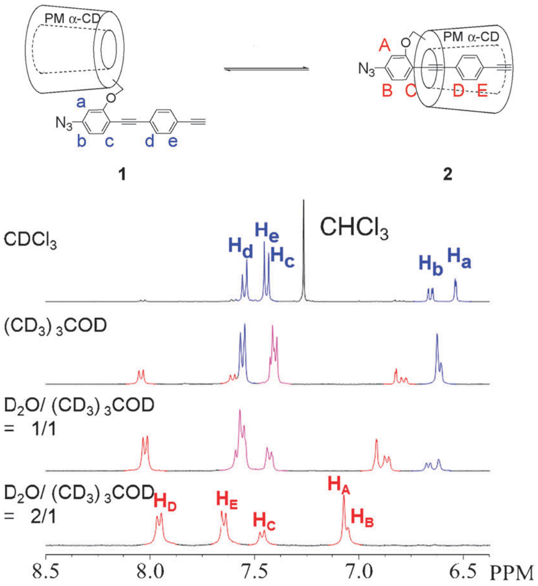
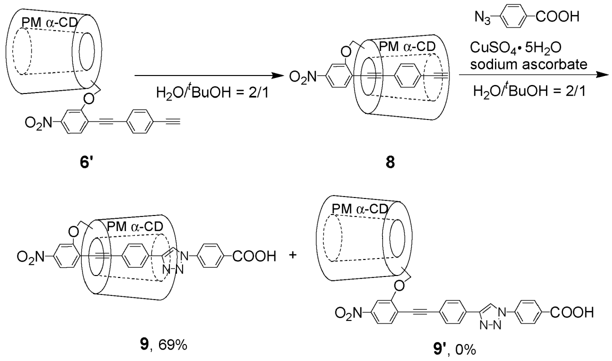


Fig. 1 Aromatic region of 400 MHz ^{1}H NMR spectra of **1** and/or **2** in several solvents at 25 °C (1) $CDCl_3$, (2) $(CD_3)_3COD$, (3) 1 : 1 D_2O : $(CD_3)_3COD$, and 2 : 1 D_2O : $(CD_3)_3COD$.

H_{a-A} (+0.53 ppm), H_{b-B} (+0.41 ppm), H_{c-C} (+0.02 ppm), H_{d-D} (+0.41 ppm), and H_{e-E} (+0.20 ppm). The remarkably large downfield shifts of H_{a-A}, H_{b-B}, or H_{d-D} suggest that the protons are located very close to the α-1,4-glucosidic oxygen atoms of PMCD or methoxy groups by self-inclusion.[21]

Confirmation of the fixed inclusion state by capping the end of the guest moiety with a π-conjugated unit bearing an azide group was further supported by the synthesis of compound **6′**, which was formed by deprotection of the silyl group of **6** after **6′** was treated with *p*-azidobenzoic acid under Cu-catalysed click reaction conditions in H_2O : *t*BuOH = 2 : 1 solution (Scheme 3). Formation of the fixed [2]rotaxane (**9**)[22] was inferred from the MALDI-TOF mass spectrum, which displayed a strong signal at *m*/*z* 1642 corresponding to the [**9** + Na]$^+$ ion. Notably, no evidence for the formation of the uninsulated compound (**9′**) was detected by NMR analysis of the crude product. Compound **9** was purified by silica gel column chromatography and obtained in pure form in 69% yield. Owing to NOEs between the protons in the π-conjugated guest moiety and the H_3 and H_5 protons in the interior of the PMCD, the structure of inclusion complex **9** was characterized by 2D ROESY NMR (Fig. S1 in the ESI‡).



Scheme 3 Synthesis of fixed [2]rotaxane (**9**).

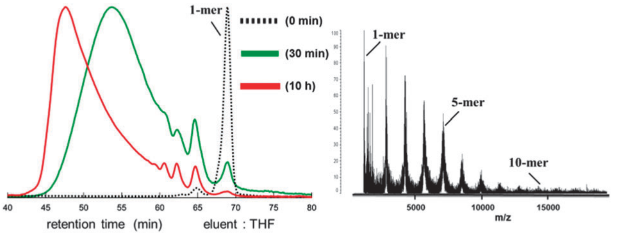


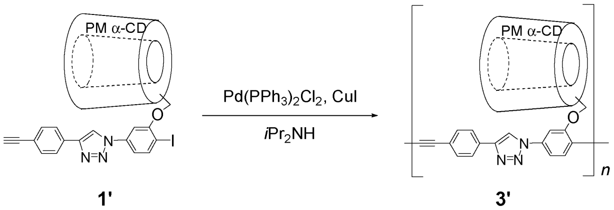
Fig. 2 (a) GPC analysis of monomer **1** and IMW **3**; (b) MALDI-TOF mass spectrum of IMW **3**.

Next, we conducted polymerization of monomeric linked [2]rotaxane (**2**) *via* a Cu-catalyzed click reaction in H_2O : *t*BuOH = 2 : 1 solution. As shown in Fig. 2a, GPC analysis revealed that monomer **2** almost completely disappeared after 10 h and formation of the IMW **3** (M_w = 1.00 × 10^5, $\tilde{n}$ = 70) was confirmed. The MALDI-TOF mass spectrum of **3** provided additional evidence for the structural authenticity of this compound. As expected, all of the observed peaks in the mass spectrum corresponded to singly charged molecular ions containing more than ten repeating units (Fig. 2b). Studies conducted using space-filling models (Fig. S2, ESI‡) revealed that the covering ratio of PMCDs in the backbone of **3** was approximately 80%.

To synthesize uninsulated polymer as a reference for IMW **3**, we carried out click polymerization of uninsulated monomer **1** in a hydrophobic (*i*Pr_2NH) instead of a hydrophilic (H_2O : *t*BuOH = 2 : 1) solution under similar click reaction conditions to those used for the synthesis of **3**. The uninsulated polymer was obtained in low yield along with a significant amount of undesired products, probably *via* 1,4- and/or 1,5-addition, since it is known that the click reaction sometimes does not proceed selectively and efficiently in non-aqueous solutions.[23,24] We then polymerized **1′** by Sonogashira reaction, which efficiently proceeds in hydrophobic solution, and succeeded in synthesizing uninsulated polymer **3′** (Scheme 4) (M_w = 1.00 × 10^5, $\tilde{n}$ = 16) having the same main chain structure formed by click polymerization of **1**.

To evaluate the covering effect of PMCD, we compared the absolute fluorescence quantum yield of **3** and **3′** using a calibrated integrating sphere system. As expected, IMW **3** (Φ_{solution} = 0.37, Φ_{solid} = 0.06) indicated higher photoluminescence efficiencies as compared to uninsulated polymer **3′** (Φ_{solution} = 0.07, Φ_{solid} = 0.02) in both solid and solution states, suggesting that to attain efficient fluorescence properties, encapsulation of the chromophore by PMCD is essential.

Next, we examined the potential for photo-induced charge separation and the transport properties of the IMW in the



Scheme 4 Synthesis of uninsulated polymer **3′**.

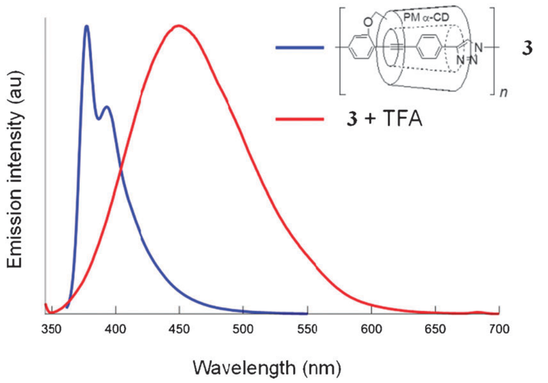


Fig. 3 Photoluminescence spectra of **3** before and after protonation.

solid state by simultaneously carrying out *in situ* flash photolysis time-resolved microwave conductivity (TRMC) and transient absorption spectroscopy (TAS) measurements.[25-27] The solid films of **3** show clear conductivity transients upon pulse exposure with slow recombination processes (Fig. S3a and b, ESI‡), which is in contrast to the rapid recombination of charge carriers within the time constant of TRMC measurement ($\sim$20 ns) for solid films of **3′**. TAS of an identical film resulted in simultaneous bleaching and absorption with an isosbestic point (Fig. S3c, ESI‡), and the absorption maximum shifted slightly toward the longer region ($\lambda_{\max}$ = 620 nm) with a smaller extinction coefficient ($\varepsilon^{+} = 1 \times 10^{5}$ cm^{-1} mol^{-1} dm^{3}) than those observed for radical cations of poly(phenylene ethynylene) (PPE) core molecules.[14] On the basis of the optical parameters and transient conductivity,[14,25] the values of anisotropic hole mobility in the backbones of **3** and **3′** were estimated to be 7×10^{-3} and 4×10^{-3} cm^{2} V^{-1} s^{-1}, respectively. Although these values of intramolecular mobility are lower than those of previously synthesized IMWs having a PPE core, in general, these are very high in π-conjugated polymers and comparable to those of polythiophenes.[26] The major difference in the transient conductivity over one order of magnitude is due to photo-carrier generation ($\phi = 4 \times 10^{-3}$ and 9×10^{-4} for **3** and **3′**, respectively), which is highly dependent on the presence of the insulating PMCD clads. In contrast to optical properties of the π-conjugated core of IMW without azide moieties,[14] the smaller oscillator strength of the transient absorption of radical cations suggests localization of holes on the conjugated segments divided by azide moieties; this results in equivalent values of the short range hole mobilities in **3** and **3′**, as probed by TRMC measurement.

The CH_3OH solution of **3** emitted blue light and its photoluminescence (PL) peaks were red-shifted upon the addition of trifluoroacetic acid (TFA), indicating an acidichromic effect.[28] The PL spectra of **3** before and after protonation are shown in Fig. 3. Emissions of **3** in CH_3OH are narrow and structured owing to its well-defined excited state. The protonation of its triazole rings at the 3-position by TFA bathochromically shifts its emission to 455 nm and broadens its PL spectrum owing to the acid-caused perturbation of its excited state. Because of this unique phenomenon, IMWs of **3** are potentially applicable as monomolecular electronic materials to enable conductivity switch by acidity.

In conclusion, we developed new methods for the syntheses of highly organic-soluble IMWs with PMCD lines in the same direction by carrying out click polymerization of linked [2]rotaxane monomers. The obtained IMWs had high solubility in organic solvents and a high covering ratio, rigidity, and photoluminescence efficiency. Experiments are currently being performed to evaluate the behaviour of the new material in molecular electronics.[29]

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