

FOCUS REVIEW

Stimuli-responsive functionalized insulated conjugated polymers

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Diverse functionalized insulated conjugated polymers (ICPs) were synthesized via co-polymerization between insulated conjugated monomers and various functional units. Such polymers possessed well-defined, linked-rotaxane structures with target-specific insulations through a fine-synthetic technique. The functional moieties on the polymer backbones strongly affected their π -conjugation, which afforded sensitivity toward external stimuli. Chemical and physical inputs, such as redox, light, ions and gases, could be detected by modulating their optical and electrical properties. Moreover, the linked-rotaxane insulating structures inhibited undesired π - π interactions between chains and prohibited thermal fluctuation in the conjugated backbones. The rotaxane structures efficiently enhanced the processabilities and physical properties of the sensing materials. Accordingly, cooperative effects were observed between the insulation and functional moieties in functionalized ICPs. In this review, sophisticated material designs and synthetic strategies toward functionalized ICPs will be described with a focus on reversible sensing of external stimuli.

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INTRODUCTION

Recently, new materials with unique functionalities and properties have been eagerly pursued owing to increasing societal and industrial demands. Finely synthesized organic polymers are advantageous for the demands directed toward flexible and light materials with high tunabilities and processabilities.^{1,2} Specifically, π -conjugated polymers have garnered considerable interest due to their unique optical and electrical functionalities, which are useful in applications such as light-emitting diodes,^{3,4} solar cells^{5,6} and biosensors.⁷ However, their applications in some practical materials are limited due to several issues including the strong π -interactions between conjugated chains, which decreases their solubility and processability. Moreover, in the solid state, disordered energy/electron transfers can dramatically affect their physical properties.⁸ In order to improve their processability and physical properties, insulated conjugated polymers (ICPs), where their conjugated chains are covered with protective cyclic molecules, have been investigated for a few decades.^{9–11} Threading structures (that is, polyrotaxanes)¹² inhibit undesired molecular interactions to bring forth the original properties of the isolated π -system, even in the solid state. The unique properties of independent conjugation have been applied to optical materials¹³ and conductive components.^{14,15} However, limited research has been focused on the incorporation of various functionalities in ICPs, with the exception of the optical and electrical properties of conjugated backbones, because highly functionalized ICPs demand sophisticated synthetic strategies including organic and rotaxane chemistries.¹⁶ Accordingly, the establishments of functionalized ICPs have potential for use in unprecedented supramolecular materials.

Cyclodextrins (CDs) have been widely used for the synthesis of ICPs because of their commercial availability and high efficiency inclusions.^{17,18} Organic conjugated monomers were encapsulated in CDs under aqueous conditions to form inclusion complexes. Thus, encapsulated monomers were polymerized under the same conditions to provide typical ICPs (Figure 1a).^{19–24} Although the polymers showed high solubility in water due to the covering CDs, their low solubility in organic solvents has long been an obstacle in their processability and material applications. In particular, the organic-solvent-based synthetic techniques for functionalizations of ICPs have been limited due to their low solubility in organic solvents.

In 2009, our group developed a new synthetic methodology for permethylated CD-based ICPs with desirable material properties and high solubility in organic solvents.^{25,26} The permethylation of CDs increased their solubility in organic solvents and increased the insulating area of the threading organic molecules due to their deep vacancy. The cyclic molecules were connected with conjugated monomers, which entropically facilitated their encapsulation in aqueous media (that is, self-inclusion). The molecular design was applied to an oligo(phenylene ethynylene) (OPE) monomer bearing two permethylated α -CDs, which formed a self-inclusion complex in highly polar solvents, and subsequently polymerized to form organic-soluble ICPs. The highly insulated polymer inhibited molecular interactions between chains and displayed high intramolecular hole mobility even in the solid state.^{26,27} Such linked rotaxanes exhibited defect-free insulation;^{14,28} the cyclic molecules were fixed on the polymer backbones via a linkage, which prevented thermal shuttling, which was in contrast to conventional conjugated polyrotaxanes

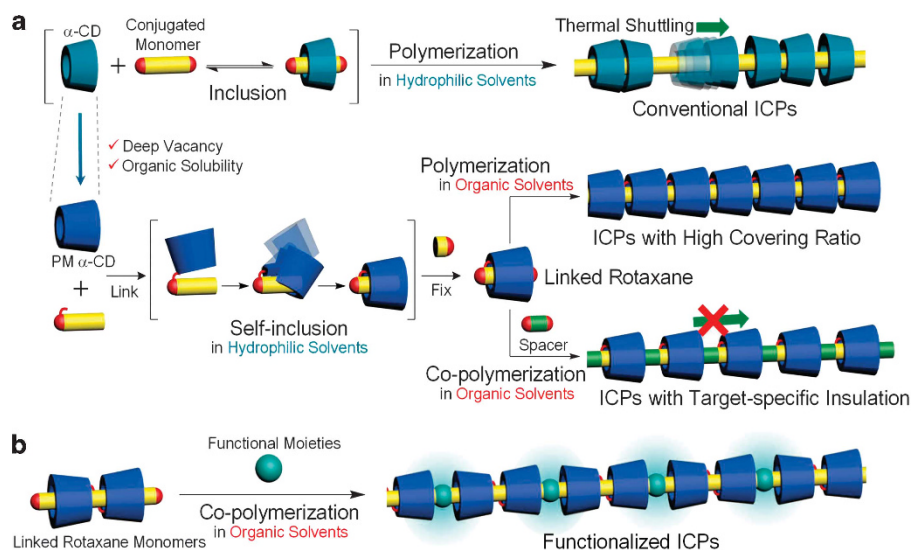


Figure 1 Synthetic strategies for (a) conventional ICPs and linked rotaxane-based ICPs bearing permethylated α -CDs (PM α -CDs) and (b) functionalized ICPs from linked rotaxane monomers.

(Figure 1a). The linked macrocycles with high covering ratios provided defect-free protection to the backbones. Furthermore, with a low covering ratio (that is, upon insertion of spacer units), the cyclic molecule protected target-specific areas on the conjugated backbones without thermal shuttling.²⁹ The specific structures in the linked rotaxanes contributed to the unique material properties. The intramolecular high conductivity of the ICPs was successfully applied to molecular wiring materials in a molecular electronics field.³⁰ The insulated structures improved the wiring efficiency between nano-electrodes.¹⁵ Moreover, molecular modification of the ICPs improved the intramolecular charge mobility. The mobility reached $8.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was comparable to an amorphous silicon material, after modification of the OPE backbones.³¹

Although conductive rotaxane structures for molecular electronics have been achieved by many research groups,^{14,32,33} ICPs may have other useful functionalities peculiar to designable organic compounds. However, with the exception of their optical and electrical properties, studies regarding the functionalities of ICPs are limited due to the sophisticated synthetic strategies that are required. Towards that end, organic-solvent soluble ICPs based on linked rotaxanes are more amenable to synthetic modifications. This review summarizes recent progress in linked rotaxane-type ICPs with novel functionalities, with a focus on sensing materials, by introduction of organic and inorganic components on the conjugated polymer backbones. A reasonable synthetic strategy is proposed for the functionalization of ICPs via copolymerization in organic solvents between functionalized components and soluble insulated conjugated monomers (Figure 1b), which were prepared divergently via fixation of a linked-rotaxane precursor. Synthetic strategies and applications of stimuli-responsive ICPs are described.

DIVERGENT SYNTHESIS OF INSULATED CONJUGATED MONOMERS WITH LINKED-ROTXANE STRUCTURES

An OPE bearing two permethylated α -CDs (**1'**) was prepared via three steps from 6-*O*-monotosyl permethylated CD (Figure 2a).²⁶ The two cyclic molecules in **1'** encapsulated the conjugated backbone to form self-inclusion complex **1** by hydrophilic-hydrophobic interactions in polar solvents (Figure 2b). The self-inclusion was characterized by ¹H NMR by employing different deuterated solvents (Figures 2c–e).

Upon increasing the hydrophilicity of the solvents, the formation of inclusion complex **1** predominated; downfield-shifted peaks stemming from insulated structure **1** were observed in addition to the original peaks of **1**.^{34,35} Although **1** and **1'** were observed in CD₃OD (Figure 2d), only inclusion complex **1** was observed in more polar CD₃OD/D₂O (2/1v/v) (Figure 2e).³⁶

Sonogashira coupling reactions with iodoaryl derivatives **2a–d** were conducted in CH₃OH/H₂O to fix inclusion complex **1**, providing insulated molecules **3a–d** bearing various units at both ends (Figure 3).^{37–40} The introduced terminal groups (pyridine, terminal alkyne, bromopyridine and terpyridine) could be utilized as subsequent reaction points. Notably, with terpyridine, the formation of cation complex (bis(terpyridine)iron(II)) **2d'** was required with the iodoaryl derivative because of an intact reaction with haloterpyridine **2d'**, which could not be dissolved in the aqueous reaction solvent. The Sonogashira coupling reaction afforded oligomeric products containing the bis(terpyridine)Fe(II) complex; subsequent demetallation of Fe(II) resulted in an insulated unit bearing terpyridine moieties (**3d**) in a high yield.⁴⁰ On the other hand, in organic solvents with low polarity, rotaxane precursor **1** formed uninsulated structure **1'** and the Sonogashira coupling reaction with **2a–c** and **2d'** afforded uninsulated conjugated molecules **3a'–d'**. The fixation method for **1'** could be used to selectively and divergently synthesize insulated/uninsulated conjugated molecules **3/3'** bearing various terminal groups.^{41,42} Compounds **3** and **3'** could not be interconverted due to their long conjugated backbones and linkages.

The formed insulated structure was successfully visualized via single crystal X-ray analysis of insulated unit **4** after complexation with Rh(TTP)Cl complex (TTP: tetratolylporphyrin) and pyridyl terminated insulated conjugated molecule **3a** (Figure 4). The crystal structure indicated that two cyclic molecules were connected and covered the conjugated backbone. The three-dimensional insulation enhanced the rigidity and linearity of the OPE backbone; the dihedral angle between the two TTP planes was almost parallel (178°).

SYNTHESIS OF FUNCTIONALIZED ICPs VIA SONOGASHIRA COUPLING CO-POLYMERIZATION

The co-polymerization of insulated conjugated molecules **3** and diverse molecules provided insulated polymers with various

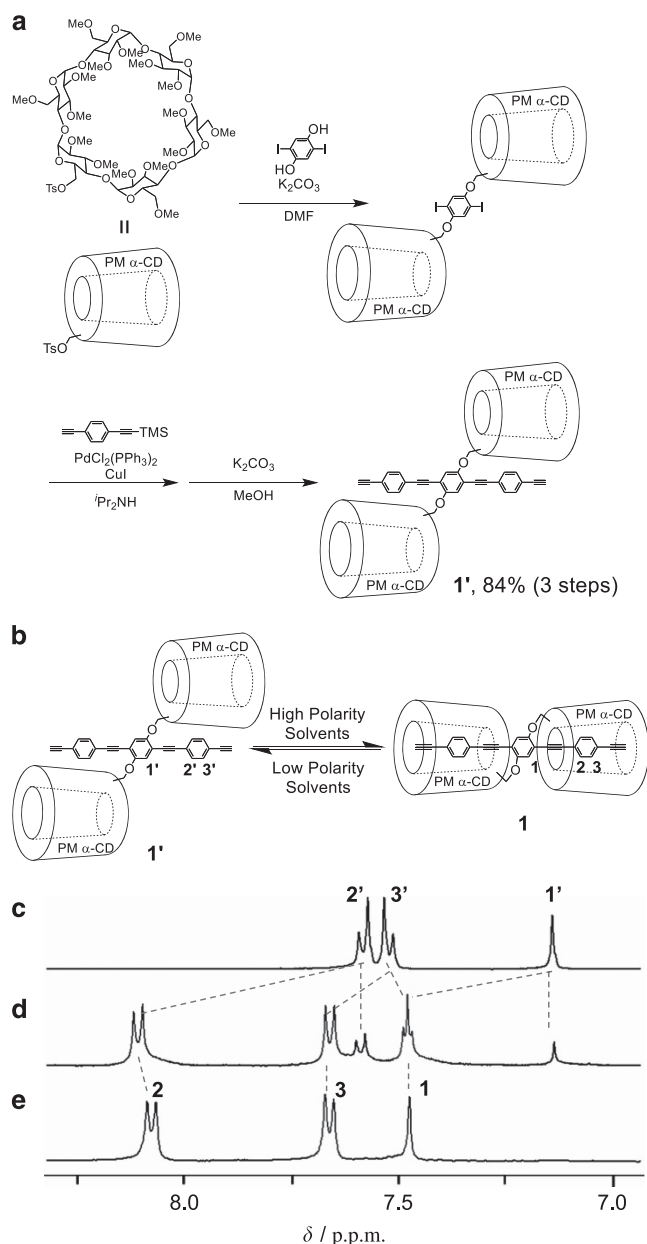


Figure 2 (a) Synthesis of permethylated α -CD (PM α -CD)-bearing OPE **1'** (Terao *et al.*,²⁶) and (b) its self-inclusion. 1H NMR spectra (500 MHz) of **1'** in (c) CD_2Cl_2 , (d) CD_3OD and (e) CD_3OD/D_2O (2/1v/v).

functionalities. Ethynyl-terminated **3b** was polymerized via Sonogashira coupling with 1,4-diiodobenzene to form insulated poly(phenylene ethynylene) **5** ($M_w = 1.2 \times 10^5$, $M_n = 3.8 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by size-exclusion chromatography (SEC).) (Figure 5).³⁸ The polymerization increased the effective conjugation length, which enhanced the emission and conductive properties. The intramolecular charge mobility of **5** was measured with an electrodeless technique through time-resolved microwave conductivity with transient absorption spectroscopy.⁴³ A high charge mobility ($0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was obtained even in the solid state, since the insulation prohibited disordered charge hopping between conjugated species. Sonogashira coupling polymerization with **3b** could also be

applied to functionalized molecules bearing dihalobenzene moieties. Desired functionalities could be introduced onto insulated polymers by tuning the molecular structures of the dihalobenzenes. Polymerization with 4,7-dibromo-2,1,3-benzothiadiazole provided **6** ($M_w = 8.4 \times 10^5$, $M_n = 2.0 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC), which exhibited an absorption band in the long-wavelength region. Its narrow energy gap was attributed to its donor-accepter type π -conjugation.

STIMULI-RESPONSIVE ORGANIC-FUNCTIONALIZED ICPS

Redox-responsive conjugated polymer **7-red** ($M_w = 1.6 \times 10^5$, $M_n = 4.2 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) was obtained by introduction of tetrathiafulvalene as a redox-active moiety⁴⁴ through co-polymerization between insulated monomer **3b** and diiodotetrathiafulvalene. Polymer **7-red** was oxidized with $Fe(ClO_4)_3$, which led to a dramatic increase in its fluorescence intensity in $CHCl_3$. Treatment of **7-ox** with reducing reagent $FeCp_2$ led to a decrease in the emission. The drastic changes in fluorescence were attributed to changes in the orbital energy relationship between redox-active tetrathiafulvalene and insulated OPE. The corresponding uninsulated polymer **7-red** ($M_w = 9.4 \times 10^4$, $M_n = 3.7 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) exhibited smaller changes in fluorescence in response to redox stimuli, indicating that the insulation enhanced the redox-sensitivity. Moreover, light-responsive diiododiarylethene was co-polymerized with insulated monomer **3b**. The diarylethene cleaved its π -conjugated system in **8-o** ($M_w = 9.4 \times 10^4$, $M_n = 3.7 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) via isomerization under UV irradiation⁴⁵ and conjugated polymer **8-o** was converted into a less conductive polymer. This photo-switching response was reversible; the localized conjugation of irradiated polymer **8-c** could revert to the initial state upon irradiation with visible light. The switching polymer was applied to molecular wiring materials between 20 nm gapped electrodes.⁴⁶

Insulated polymer **9-Zn** ($M_w = 2.1 \times 10^5$, $M_n = 5.3 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) bearing a Zn-porphyrin moiety was prepared via co-polymerization between alkyne-terminated monomer **3b** and dibromo-Zn-porphyrin. The corresponding free-base porphyrin polymer **9-H₂** was obtained following demetallation of **9-Zn** with TFA. Zn(II) ions could be re-introduced on the free-base porphyrin. Moreover, Fe(II) ions were inserted into **9-H₂** via metal salts and treatment with CO gas. The conductivities of the conjugated backbones were evaluated using time-resolved microwave conductivity with transient absorption spectroscopy measurement. The mobility of the hole carrier on the Fe(II)-porphyrin polymer **9-Fe** was enhanced as compared with that of Zn(II)-one **9-Zn**. The intramolecular charge mobility on the polymer backbone was estimated to be $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; a highly conductive backbone was constructed through the Fe porphyrin. The conductivities depended on the metals and could be applied to metal sensors in the field of molecular electronics.

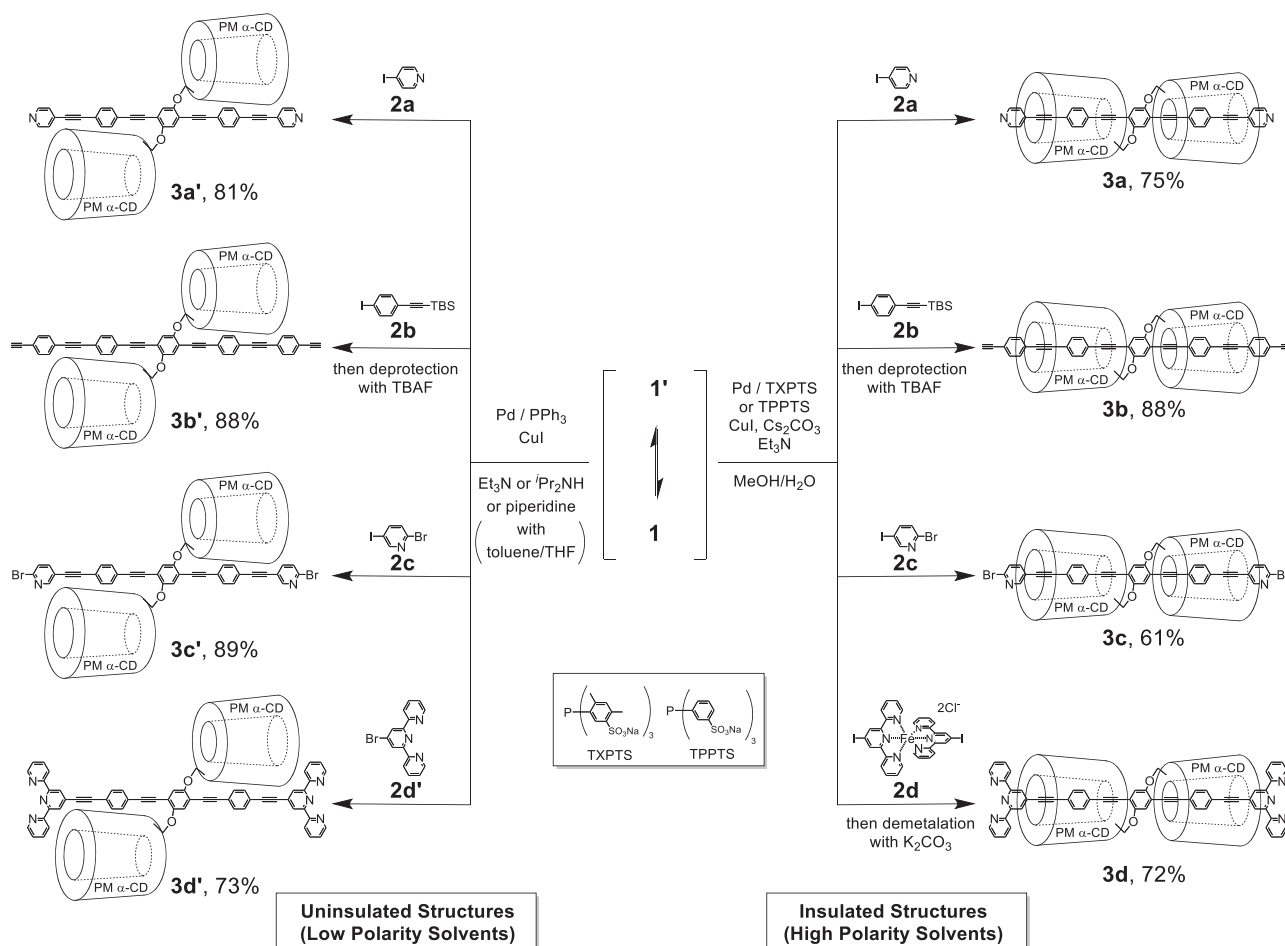


Figure 3 Divergent syntheses of insulated/uninsulated units **3** and **3'**.^{37–40}

OPTICAL SENSORS BASED ON FUNCTIONALIZED ICPS

Next, ICPS were applied as optical ion sensors. The optical properties of conjugated polymers are governed by their π -conjugation systems; the alteration of their molecular orbitals by external stimuli affects their optical properties, making them useful materials for optical sensors. For example, ICPS with triazole moieties, brønsted bases, were constructed via Huisgen cyclization.⁴⁷ The nitrogen atoms interacted with brønsted acid (trifluoroacetic acid); the absorption spectrum was dramatically altered following the ion recognition.

Multiple metal-ions could be selectively identified using a single polymer.³⁹ Insulated polymer **10** ($M_w = 1.1 \times 10^5$, $M_n = 5.3 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) bearing bipyridyl groups was synthesized via palladium catalyzed Stille–Kelly coupling polymerization of **3c** (Figure 6). The cyclic molecules were fixed on the polymer backbones with linkages so that the bipyridyl units in **10** were selectively exposed to the external environment. Polymer **10** displayed blue fluorescence even in the film state, because cyclic molecules on the OPE prohibited molecular interactions in the solid state (Figure 6a). This was in contrast to naked polymer **10'** ($M_w = 1.0 \times 10^5$, $M_n = 4.9 \times 10^4$), (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) which exhibited quenched fluorescence in the solid state. Moreover, in target-specific insulated polymer **10**, bipyridyl groups were selectively uninsulated, so that they could

connect interact with metal ions. Coordination with typical metal chlorides ($ZnCl_2$, $CdCl_2$, $InCl_3$, $GaCl_3$ and $SnCl_4$) altered the molecular orbital to provide a narrow energy gap due to the Lewis acidity of the metal chlorides;⁴⁸ the changes in the molecular orbital energy of π -conjugated systems depended on the valency of the metal. The emission colors of the polymer films changed from blue to green and yellow upon coordination with typical metal ions (**10-Zn**, **10-In** and **10-Sn**; Figure 6a). The tin-coordinated insulated polymer **10-Sn** displayed a high fluorescence quantum yield ($\Phi_{FL} = 46\%$) even in the film state. As an application, polymer film **10** coated on an SiO_2 substrate was dipped step-wise in ion solutions ($SnCl_4$ and $InCl_3$ in Et_2O) for 5s (Figure 6b). The emission of the dipped area changed to yellow (**10-Sn**) and green (**10-In**). After removal of the ions with ammonia, the emission and coordination ability returned to their initial states. Accordingly, polymer film **10** served as a reversible sensor for typical metal ions.

INORGANIC FUNCTIONALIZED ICPS WITH SENSING ABILITIES BASED ON COORDINATION TO TRANSITION METALS

Novel functionalities of insulated polymers were achieved using transition metals, which are known for their unique properties based on triplet species^{49,50} and reversible coordination bonds.⁵¹ Insulated units bearing coordinative terminal ends could be regarded as insulated bridging ligands. Namely, coordination polymers were synthesized via one-dimensional complexation between insulated bridging ligands and transition metal complexes.⁵² Thus, introduced

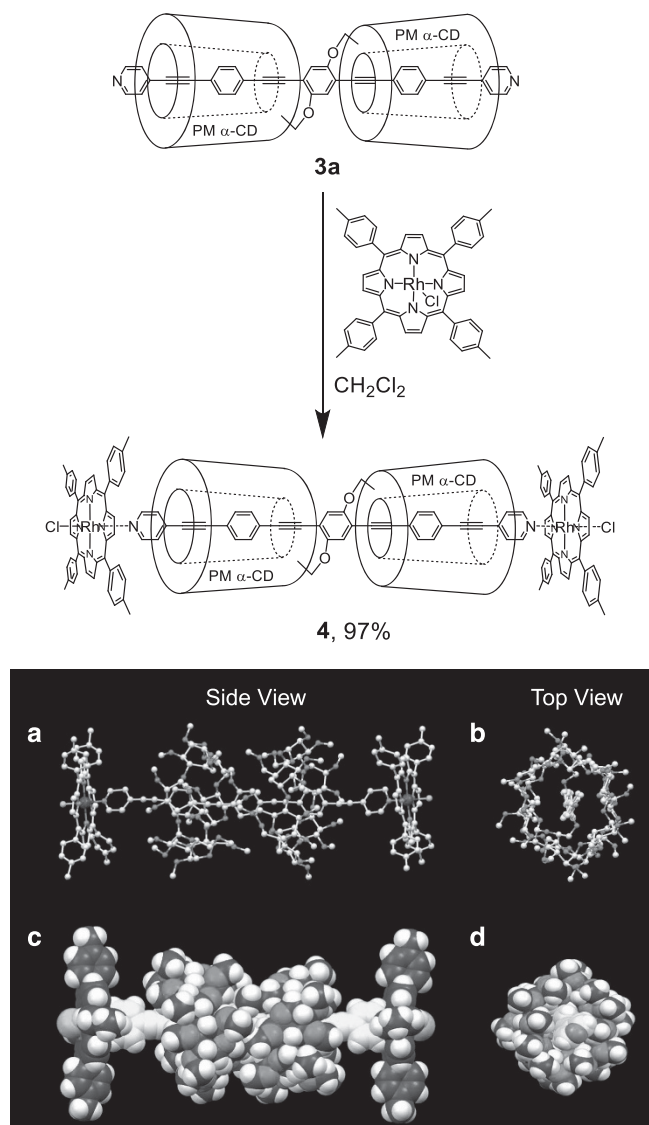


Figure 4 Synthesis of **4** and its single crystal structure.³⁷ (a, b) ball and stick model, and (c, d) CPK model. In b, d, the Rh-porphyrin moieties were omitted for clarity. Adapted with permission from Masai *et al.*³⁷. Copyright 2014 the American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

transition metals strongly affected the π -conjugated upon direct insertion in the polymer backbone.^{53,54}

Terpyridine-bearing insulated molecule **3d** was polymerized with Fe(II), Ni(II), Co(II) and Ru(II) complexes (Figure 7a).⁴⁰ The polymerizations were confirmed by a SEC and by the metal to ligand charge transfer transition in the absorption spectrum. The high intramolecular charge mobility ($0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) mediated by the Fe(II)-bisterpyridine moieties in **11-Fe** ($M_w = 2.2 \times 10^5$, $M_n = 1.5 \times 10^5$) (M_w and M_n were calculated by polystyrene standard calibration after separating the high-molecular-weight fractions of polymers from reaction mixtures by SEC) was confirmed by time-resolved microwave conductivity with transient absorption spectroscopy measurement. The redox state of the Fe(II)-terpyridine complexes could be modulated by chemical stimuli. The Fe(II) moiety in the coordination polymer could be oxidized by cerium(IV) ammonium nitrate, as confirmed by absorption spectroscopy.⁵⁵ Thus, oxidized Fe(III)

influenced the polymeric constitution. The coordination of Fe(III) with two terpyridine units resulted in the decomposition of the coordination polymer into bridging ligands and metals, as confirmed by SEC. The mixture was re-polymerized under reductive conditions, indicating its reversible response towards chemical redox stimuli.

Pyridyl-terminated insulated bridging ligand **3a** was polymerized with Ru(II) porphyrin to form Ru-containing conjugated polymer **12** ($M_w = 7.1 \times 10^4$, $M_n = 2.7 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration of reaction mixtures. The high-molecular-weight fractions of polymers were separated by SEC and used for the following analyses) (Figure 7b).³⁷ The Ru porphyrin fixed the two pyridyl groups of **3a** in the *trans*-configuration, forming a one-dimensional coordination polymer. Ru-N bonds were formed under UV irradiation and the carbonyl ligands were eliminated from the Ru porphyrins as CO gas.⁵⁶ Insulated polymer **12** possessed high rigidity due to its macrocyclic fixation on the backbone. Polarized optical micrographic observations revealed that in CHCl_3 , the insulated polymer solution formed a cholesteric liquid crystal phase (Figure 7c), whereas the corresponding uninsulated polymer did not. The insulation enhanced the rigidity and linearity of the conjugated polymer backbone.

Notably, its backbone is composed of coordination bonds, so that a reversible monomer-polymer interconversion could be successfully realized under specific external stimuli. Ru-pyridyl coordination bonds in **12** were decomposed under 1 atm CO gas to form monomers (bridging ligand **3a** and Ru porphyrin).⁵⁷ Under UV irradiation, re-polymerization resulted in polymer **12** ($M_n = 2.7 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration of reaction mixtures. The high-molecular-weight fractions of polymers were separated by SEC and used for the following analyses) owing to the coordination between Ru and pyridine after the release of CO gas. In addition to the reversible formation of the coordination polymer, polymer **12** showed interesting electrical properties due to the Ru complex. Time-resolved microwave conductivity with transient absorption spectroscopy measurements revealed that the Ru(II)-containing polymer had a high intramolecular charge mobility along the conjugated backbone through the metal complexes; the intramolecular charge mobility ($0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was comparable to those of purely organic conjugated polymers. According to computational studies, the high mobility was derived from the buffering effect of the Ru-pyridyl coordination bonds on the thermal fluctuation along the polymer backbone.⁵⁸ Moreover, the time course of the conductivity after excitation demonstrated the very long carrier lifetime ($\sim 1 \text{ ms}$) of the triplet state based on the heavy atom effect of Ru(II). The results demonstrated that the triplet excited state could be active over a long timescale even in the solid state, due to the protection of the cyclic molecules.

PHOSPHORESCENT ICPS WITH COVALENTLY BONDED TRANSITION METALS

Insulated metal-containing polymers have been applied as phosphorescent materials. Utilizing the stable triplet state would provide polymers with solid-state phosphorescence. A Pt-acetylide complex was inserted into an ICP as the phosphorescent moiety⁵⁹ via Cu-catalyzed co-polymerization between an alkynyl-terminated monomer and a Pt complex under aqueous conditions (Figure 8a).³⁶ The corresponding uninsulated polymer **13'** ($M_w = 1.6 \times 10^5$, $M_n = 4.3 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration of reaction mixtures. The high-molecular-weight fractions of polymers were separated by SEC and used for the following analyses) a structural isomer of the insulated

phosphorescence quenching in solid polymers. Moreover, identical photo-physical properties, that is, wavelength and quantum yield, were observed in the solid state ($\lambda_{\max} = 581$ nm, $\Phi_{\text{PL}} = 4.4\%$) as compared with the dilute solution ($\lambda_{\max} = 585$ nm, $\Phi_{\text{PL}} = 5.4\%$) due to the perfect insulation of polymer **13**.

Further systematic investigations were carried out in order to clarify the details of such cyclic insulation effects. Although cyclic molecules in conventional rotaxanes could thermally shuttle on the axles, macrocycles in the linked rotaxanes were fixed on the polymer by linkages. Namely, the linked rotaxanes could selectively protect a target-specific area (Figure 8c). The centers of the OPE conjugations were protected in polymer **14** ($M_w = 3.1 \times 10^5$, $M_n = 4.6 \times 10^4$), whereas the Pt complexes were covered in polymer **15** ($M_w = 6.6 \times 10^4$, $M_n = 2.2 \times 10^4$), and they possessed the same covering ratios on the backbones (M_w and M_n were calculated by polystyrene standard calibration of reaction mixtures). The high-molecular-weight fractions of polymers were separated by SEC and used for the following analyses). Polymer **16** ($M_w = 1.2 \times 10^5$, $M_n = 3.1 \times 10^4$) (M_w and M_n were calculated by polystyrene standard calibration of reaction mixtures). The high-molecular-weight fractions of polymers were separated by SEC and used for the following analyses) had more extensive π -conjugation than polymer **13** with the same insulation degree as polymer **13**. The effects of insulation on phosphorescence were investigated by comparing these polymers. In dilute solutions,

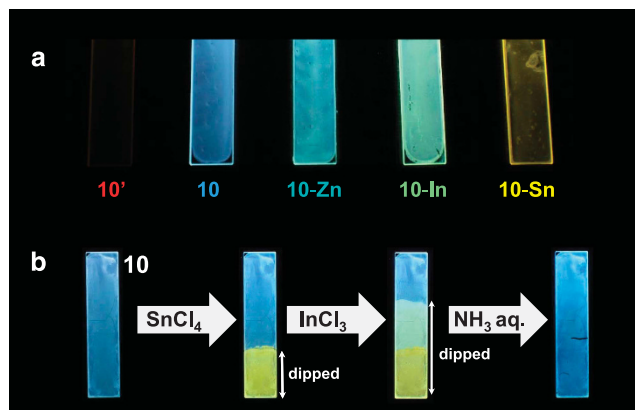
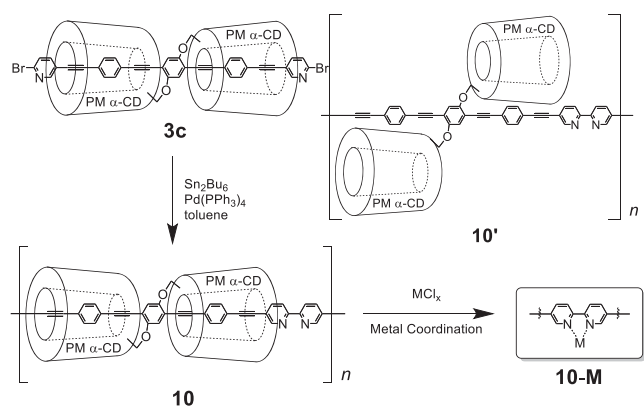


Figure 6 (Top) Chemical structures of insulated/uninsulated bipyridine-based polymers **10/10'** and synthetic scheme of **10-M**.³⁹ (Bottom) Emission under 365 nm irradiation of (a) polymer films (**10'**, **10**, and **10-M**) coated on SiO_2 substrates and (b) reversible multi-metal sensibility of polymer **10** film on SiO_2 substrate via sequential dipping into ion solutions (SnCl_4 and InCl_3 in Et_2O) and aqueous ammonia. Adapted with permission from Hosomi *et al.*³⁹. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

polymer **14** displayed stronger phosphorescence than **15**, indicating that the effect of insulation on the thermal fluctuation depended on the area. Insulating the center of phenylene ethynylene effectively

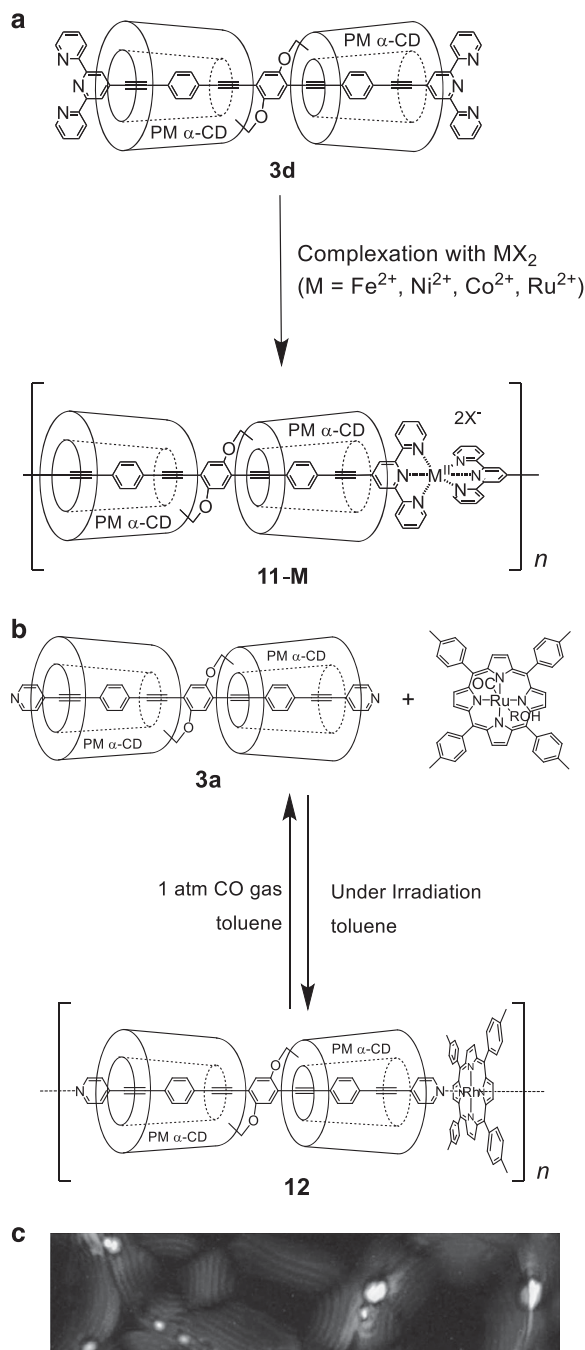


Figure 7 Synthetic schemes of insulated coordination polymers (a) **11-M**⁴⁰ and (b) **12**.³⁷ (c) Polarized optical micrograph of polymer **12** in CHCl_3 . Adapted with permission from Masai *et al.*³⁷. Copyright 2014 the American Chemical Society.

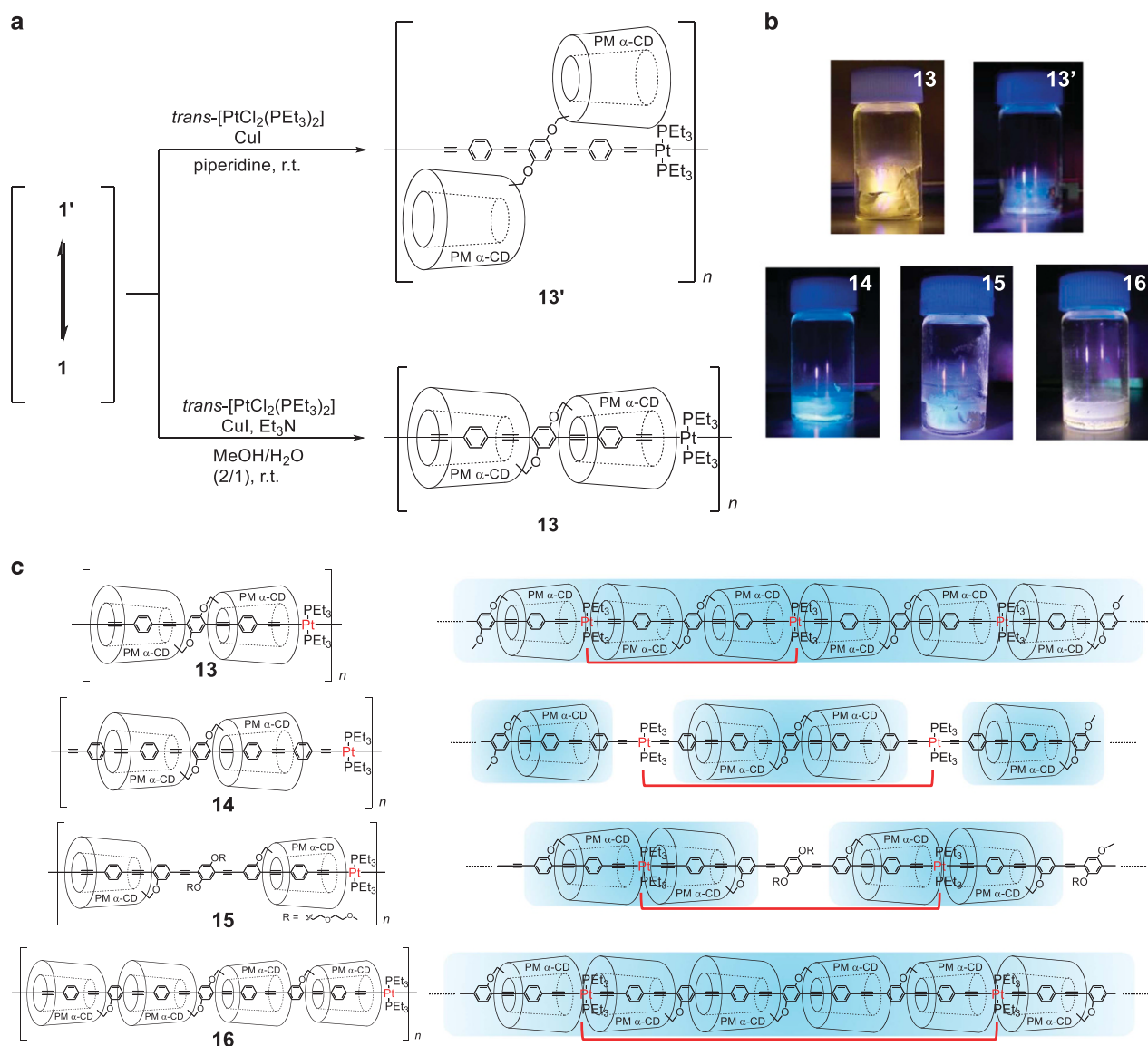


Figure 8 (a) Synthetic routes towards ICP **13** and insulated **13'**.³⁶ (b) Emission of polymer films (**13**–**16** and **13'**) under irradiation at 365 nm and an argon atmosphere.⁶⁰ (c) Chemical structures of polymers **13**–**16** and depiction of insulation areas and ratios. Red lines indicate the repeating units of the polymers. Adapted with permission from Masai *et al.*⁶⁰. Copyright 2014 the American Chemical Society.

enhanced the phosphorescence intensity in the Pt-acetylide polymer. In the solid state, partially insulated polymers **14** and **15** did not exhibit orange phosphorescence in the solid state, but only showed blue fluorescence. On the other hand, completely insulated polymer **16** displayed weak phosphorescence even in the solid state (Figure 8b). Accordingly, a high covering ratio without exposed organic and inorganic areas was required for solid state phosphorescence.

CONCLUSION AND OUTLOOK

In summary, functionalized conjugated polymers insulated with permethylated α -CDs exhibit interesting responses towards external stimuli. Insulated and uninsulated structures were selectively synthesized from single precursors with iodoaryl derivatives by changing the polarity of the solvent. Monomers bearing terminal reaction points were polymerized with functional moieties. Such functionalization led to changes in their absorption and emission, as well as reversible responses towards external stimuli. The inputs reversibly affected the

conjugated backbones, which influenced the optical properties and conductivities of the polymers upon exposure to various stimuli, such as redox, light, ions, and gases. The responses could be applied in polymer films and molecular electronic materials for sensing. Moreover, the insulated structures exhibited improved physical and sensing properties in addition to processabilities, that is, the cooperative effects between insulation and functionalized moieties. Further applications may be possible through the fusion of organic/inorganic units and other insulated conjugated backbones, such as insulated polyphenylenes and polythiophenes.⁶¹ Moreover, highly conductive and sensing ICPs could be applied in polymer electronic materials via polymerization between nano-electrodes. Currently, material designs based on insulated polymers are being developed, and new covalently linked-rotaxane structures have provided conventional materials with unprecedented properties owing to their site-selective insulation and inhibited molecular thermal fluctuations.

Further progressive developments could be directed toward diverse fields in materials science using functionalized ICPs.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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