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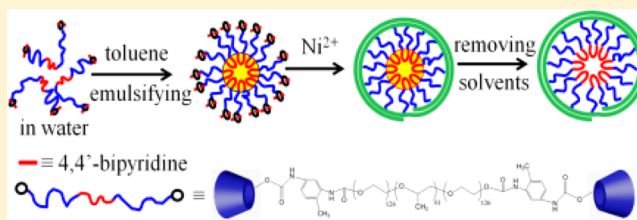
Synthesis and Characterization of Nanowire Coils of Organometallic Coordination Polymers for Controlled Cargo Release

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S Supporting Information

ABSTRACT: Nanowire coils of organometallic coordination polymers have been synthesized for the first time by using the emulsion periphery polymerization technique. An amphiphilic triblock copolymer terminated with inclusion complex of β -cyclodextrin and 4,4'-bipyridine self-assembles into oil-in-water emulsion in a toluene/water mixture. Subsequent coordination of bipyridine with Ni(II) in periphery of emulsions results in the formation of coordination polymer nanowire coils. The nanowire coils are composed of nanowires with diameter of 2 nm. Nanowire coils exhibit enhanced thermal stability in contrast to their parent triblock copolymer. Interestingly, nanowire coils are capable of encapsulating organic cargoes. Encapsulated cargoes can be selectively extracted from nanowire coils without damaging nanowire coils. Nanowire coils are potential candidates for encapsulating and controlled release of organic cargoes.



1. INTRODUCTION

The synthesis of complex hybrid nanostructures is crucial for fabricating high-performance nanodevices in the future.¹ The main challenges lie in controlling of the alignment of component nanoparticles and fundamentally understanding the correlation between morphology and performance of complex nanostructures. In the past a few decades, the synthesis of complex nanostructures based on carbon nanotubes and DNA has been extensively investigated.^{2–4} In contrast, there are limited studies on *in situ* synthesis of complex nanostructure, especially highly anisotropic hybrid nanowires. In this regards, it is difficult to direct the growth of nanostructures at multiple scales by using conventional soft templates owing to harsh synthetic conditions such as high vacuum and temperature.

Self-assembly of polymers is emerging as one of versatile approaches to synthesize complex nanostructures with controlled morphology.^{5–8} To date, complex nanostructures with varied morphologies such as supermicelles, chains, tiny flowers, nanoribbons, and so on have been achieved.^{9–23} Manners and co-workers have synthesized supermicelle architectures through self-assembly of amphiphilic cylindrical triblock comicelles of poly(ferrocenyldimethylsilane)-based copolymers, driven by minimizing the surface free energy of the system.^{24,25} Muller and co-workers have synthesized hierarchical nanostructures of particle chains from multi-compartment micelles of block copolymers.^{26,27} In a previous work, we have synthesized tiny flowers of organometallic coordination polymers induced by crystallization of polyethylene terminated with cyanoferrate complex in solution.¹⁷ Complex nanostructures exhibit enhanced properties and various functionalities, depending on the composition and

morphologies, as demonstrated by experimental and theoretical results.^{5–27} Therefore, exploring complex nanostructures with novel morphologies is crucial for fundamentally understanding the relationship between morphology and properties of complex nanostructures.

Emulsion is a suspension of oil droplets in water, which offers a promising template for large-scale synthesis of complex nanostructures.^{28–32} However, emulsion droplets are metastable. When conditions change such as concentration, pH value, or temperature fluctuate, emulsion droplets disassemble or deform. Therefore, stabilizing the emulsion droplets is crucial for synthesis of well-defined complex nanostructures. Previously, Liu and co-workers synthesized polymer rotaxane from inclusion complex of β -cyclodextrin (β -CD) and 4,4'-bipyridine via coordination with nickel(II) ions.^{33,34} This offers a new opportunity for stabilizing emulsion droplets. Herein, we reported *in situ* synthesis of coordination polymer nanowire coils using the emulsion periphery polymerization technique.³² An amphiphilic triblock copolymer terminated with inclusion complex of β -cyclodextrin and 4,4'-bipyridine was allowed to self-assemble into oil-in-water emulsion in a toluene/water mixture. The water-soluble inclusion complex of β -cyclodextrin and 4,4'-bipyridine was located in the periphery of emulsion droplets. Subsequent coordination of bipyridine with Ni(II) in periphery of emulsions resulted in emulsion droplets entangled with bipyridine/Ni(II) coordination polymer nanowires (coordination polymer nanowire coils), as schematically illustrated in Scheme 1. We demonstrated that the polymer nanowire coils

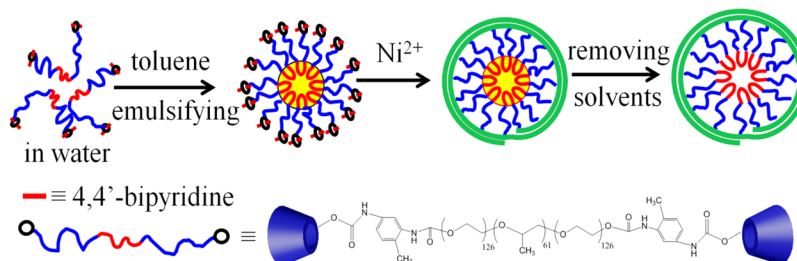
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Scheme 1. Schematic Illustration of Synthesis of Organometallic Coordination Polymer Nanowire Coils



were capable of loading organic cargoes. The encapsulated cargoes can be selectively extracted by organic solvents without damaging nanowire coils. Nanowire coils are good candidates for encapsulating and controlled release of organic cargoes. To our best knowledge, such nanowire coils of organometallic coordination polymers are unprecedented.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) ($M_n = 14\,600$ g/mol), 2,4-toluene diisocyanate (TDI), β -cyclodextrin (β -CD), 4,4'-bipyridine (bpy), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich (China) and used without further purification unless otherwise indicated.

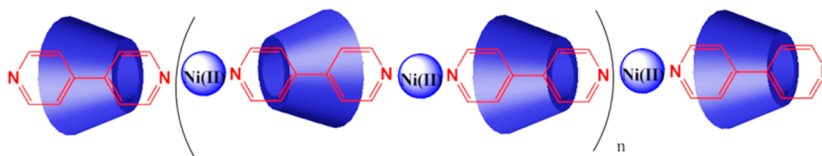
2.2. Characterization. Molecular weight and molecular weight distribution of the coordination polymers and EPE-bpy synthesized were determined using gel permeation chromatography (GPC) (Waters Breeze 2417) calibrated with polystyrene standard and with THF as eluent. Coordination polymer nanowire coil powders were dissolved in anhydrous THF with the assistance of sonication. The solution passed 200 nm filters prior to GPC measurements. A field-emission scanning electron microscope (SEM) (Hitachi S4800) was used to examine the morphologies of nanowire coils. Nanowire coils dispersed in distilled water were dip-coated on freshly polished copper stoppers. The specimens were coated with a gold/platinum alloy thin film prior to observation. A field emission gun TEM microscope (TEM2010HR) equipped with an Oxford instrument UTW ISIS EDX system was used to characterize the microstructure of nanowire coils. The acceleration voltage was 200 kV. The sample was prepared by drying a drop of nanowire coils/water suspension on a carbon-coated copper grid. The specimen was directly observed without staining due to the presence of metal elements. Tapping mode AFM to further characterize the morphology of the nanowire coils was performed using a commercial atomic force microscope (SPM-9500J3) with a silicon microcantilever (spring constant 30 N/m and resonance frequency ~ 270 kHz). The scan rate varied from 0.1 to 2.0 Hz to optimize the image quality. Nanowire coils dispersed in distilled water were dip-coated on a clean mica wafer. The solvent was allowed to evaporate at room temperature. X-ray diffraction (XRD) measurements were performed using XRD diffractometer (D-MAX 2200 VPC) equipped with Ni-filtered Cu K α radiation, having a wavelength of 0.154 nm. The diffractometer was scanned in 2θ range of 1.5° – 50° , and the scanning rate used was $1.2^\circ/\text{min}$. The TGA curves were recorded using a Netzsch TG-209 thermobalance in a temperature arrange of 25 – 550°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. UV–vis spectroscopy data were obtained by use of a Hitachi U3500 at room temperature. FT-IR spectra were recorded using a Nicolet/Nexus 670 FT-IR spectropho-

tometer. Powder samples were mixed with KBr and then pressed into pellets for FT-IR measurements.

2.3. Synthesis. *Synthesis of Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) Terminated with β -CD (EPE-CD).* 1.46 g (0.1 mmol) of dry poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) ($\text{PEO}_{126}\text{-PPO}_{61}\text{-PEO}_{126}$, $M_n = 14\,600$ g/mol) in 10 mL of anhydrous DMF was added dropwise to 34.8 mg of 2,4-toluene diisocyanate (0.2 mmol) in 10 mL of anhydrous DMF under N_2 at 30°C over 2 h. The solution was stirred at 30°C for another 3 h. To the resulting solution was added 1.1 g of dry β -cyclodextrin (β -CD, 1 mmol) in 10 mL of anhydrous DMF with vigorous stirring. The mixture was stirred at 30°C for another 3 h. The resulting mixture was added dropwise into cold ethyl ether under stirring. The precipitate was collected by filtration. The crude product was dissolved in 10 mL of methanol. The insoluble solid was removed by filtration, and the filtrate was added dropwise into cold ethyl ether with stirring. The precipitate was collected by filtration and dried in a vacuum at 40°C overnight to yield β -CD-terminated poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (EPE-CD) (yield: 92%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 1.02 (m, 183H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.28–3.33 (m, 28H, H_2 and H_4 of β -CD), 3.45 (m, 122H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.55 (m, 1022H, $\text{OCH}_2\text{CH}_2\text{O}$ of EPE and H_5 of β -CD), 3.60–3.64 (m, 28H, H_3 and H_6 of β -CD), 4.44 (t, 12H, primary hydroxyl of β -CD), 4.82 (d, 14H, H_1 of β -CD), 5.65–5.70 (m, 28H, secondary hydroxyl of β -CD), 6.90–7.20 (br, 6H, Ar–H), 7.93 (s, 4H, ArNHCOO). ^1H NMR spectra of EPE-CD agreed with literature data.¹ FT-IR (KBr): ν (cm^{-1}) 2880 (C–H stretching), 1964, 1727 (C–H scissoring of phenyl ring), 1466, 1348, 1281, and 1241 (C–H scissoring), 1095 (C–O stretching).

*Synthesis of Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) Terminated with Inclusion Complex of β -CD and 1,4-Bipyridine (EPE-bpy).* To 0.86 g (0.05 mmol) of EPE-CD in 10 mL of distilled water was added 62 mg (0.4 mmol) of 4,4'-bipyridine (bpy). The mixture was stirred overnight at room temperature. The resulting mixture was extracted with dichloromethane ($50\text{ mL} \times 3$). The combined organic phase was dried with anhydrous magnesium sulfate. The solution was concentrated and added into cold ethyl ether with stirring. The solid was isolated by filtration and dried in vacuum at 40°C overnight to give EPE-bpy with yield of 90%. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 1.03 (m, 183H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.45 (m, 122H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.55 (m, 1022H, $\text{OCH}_2\text{CH}_2\text{O}$ of EPE and H_5 of β -CD), 3.60–3.64 (m, 28H, H_3 and H_6 of β -CD), 4.44 (t, 12H, primary hydroxyl of β -CD), 4.82 (d, 14H, H_1 of β -CD), 5.65–5.70 (m, 28H, secondary hydroxyl of β -CD), 6.90–7.20 (br, 6H, Ar–H), 7.80 (d, 4H, pyridine ring), 8.70 (d, 4H, pyridine ring). ^1H

Scheme 2. Structure of Bipyridine–Ni(II) Polymers



NMR spectra of EPE-bpy agreed with literature data.^{33–35} FT-IR (KBr): ν (cm^{-1}) 2880 (C–H stretching), 1964, 1727 (C–H scissoring of phenyl ring), 1595 (C=N stretching), 1466, 1348, 1281, and 1241 (C–H scissoring), 1095 (C–O stretching).

For the purpose of comparison, the inclusion complex of β -CD and 4,4'-bipyridine was also prepared according to reference protocol.^{33,34} In a typical run, a mixture of β -CD (1 mmol) and 4,4'-bipyridine (1 mmol) was allowed to react in distilled water (60 mL) with stirring for 5 h at 30 °C. The precipitate was isolated by filtration to give white powders. Yield: 56%. ^1H NMR (300 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 3.28–3.33 (m, 14H, H_2 and H_4), 3.55 (d, 7H, H_5), 3.60–3.64 (br, 14H, H_3 and H_6), 4.44 (t, 7H, O_6H), 4.80 (d, 7H, H_1), 5.65–5.70 (m, 14H, O_2H and O_3H), 7.80 (m, 4H, pyridine ring), 8.70 (m, 4H, pyridine ring). ^1H NMR (300 MHz, D_2O), δ (TMS, ppm): 3.35–3.72 (m, 42H, H_2 – H_6 of β -CD), 4.90 (d, 7H, H_1 of β -CD), 7.52 (d, 4H, pyridine ring), 8.50 (d, 4H, pyridine ring). ^1H NMR spectra of the inclusion complex of β -CD and 4,4'-bipyridine agreed with literature data.^{33–35}

Synthesis of Nanowire Coils of Organometallic Coordination Polymers. To 51 mg of EPE-bpy in 5 mL of distilled water was added 0.25 g of toluene. The mixture was homogenized with a homogenizer for 10 min in an ice–water bath. To the resulting mixture was added a prescribed amount of NiCl_2 in 0.1 mL of distilled water. The reaction mixture was stirred at room temperature overnight. The resulting mixture was centrifuged and rinsed with distilled water until the top-layer solution became clear. The solid was dried in vacuum at 40 °C overnight to yield nanowire coils of organometallic coordination polymers. ^1H NMR (300 MHz, D_2O), δ (TMS, ppm): 3.35–3.78 (m, 1050H, $\text{OCH}_2\text{CH}_2\text{O}$ of EPE and H_2 – H_6 of β -CD), 7.68 (d, 4H, pyridine ring), 8.50 (d, 4H, pyridine ring). ^1H NMR (300 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 1.02 (m, 183H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.44 (m, 122H, $\text{OCH}_2\text{CH}(\text{CH}_3)$), 3.55 (m, 1022H, $\text{OCH}_2\text{CH}_2\text{O}$ of EPE and H_5 of β -CD), 3.60–3.64 (m, 28H, H_3 and H_6 of β -CD), 4.45 (t, 12H, primary hydroxyl of β -CD), 4.81 (d, 14H, H_1 of β -CD), 5.65–5.70 (m, 28H, secondary hydroxyl of β -CD), 6.90–7.20 (br, 6H, Ar). ^1H NMR spectra of the coordination polymers agreed with literature data.^{33–35} The nanowire coils of coordination polymers were dissolved in anhydrous THF with the assistance of sonication. Molecular weight of coordination polymers was measured using gel permeation chromatography (GPC). Number-average molecular weight of the coordination polymers was determined to be 94.2×10^3 g/mol with polydispersity of 3.56. For the purpose of comparison, molecular weight of parent EPE-bpy was also measured. The number-average molecular weight of EPE-bpy was determined to be 15.5×10^3 g/mol with polydispersity of 1.31. The high molecular weight of nanowire coils as contrasting with EPE-bpy revealed that Ni/bpy coordination polymers stringed up parent polymer EPE to form supramacromolecules (Scheme 1). FT-IR (KBr): ν (cm^{-1}) 2880 (C–H stretching), 1964, 1727 (C–H scissoring of phenyl ring), 1620 (C=N stretching), 1466,

1348, 1281, and 1241 (C–H scissoring), 1095 (C–O stretching).

Synthesis of Organometallic Coordination Polymers Nanowire without EPE. For the purpose of comparison, bipyridine–Ni(II) coordination polymers (or polymeric rotaxane) were synthesized according to the literature protocol.^{33,34} In a typical run, to a 20 mL aqueous solution of inclusion complex of bipyridine and β -CD (0.1 mmol) was added dropwise 10 mL of nickel chloride (0.1 mmol) with stirring. The mixture was stirred for 7 h at 40 °C. The solvent was removed under reduced pressure, and the solid was isolated to give a green powder. The crude product was purified by recrystallization from water and dried in vacuum to give bipyridine–Ni(II) coordination polymers. ^1H NMR (300 MHz, D_2O), δ (TMS, ppm): 3.37–3.82 (m, 42H, H_2 – H_6 of β -CD), 4.90 (d, 7H, H_1 of β -CD), 7.64 (d, 4H, pyridine ring), 8.50 (d, 4H, pyridine ring). The ^1H NMR spectra of the bipyridine–Ni(II) coordination polymers agreed with literature data.^{33,34}

Encapsulating Nile Red in Nanowire Coils. The procedure for synthesis of Nile Red loaded nanowire coils was similar to that for unloaded nanowire coils, except that Nile Red/toluene solution (Nile Red weight percentage was 1.2 wt %) was used instead of toluene.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Nanowire Coils. β -Cyclodextrin (β -CD)-terminated poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (EPE-CD) was first synthesized by coupling EPE with β -CD through 2,4-toluene diisocyanate (TDI). End groups of β -CD in EPE-CD were allowed to include 4,4'-bipyridine (bpy) to afford poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) terminated by inclusion complex of β -CD and bpy (EPE-bpy). EPE-bpy was then used as surfactant to prepare oil-in-water emulsion droplets in toluene/water mixture. Upon addition of nickel ions (Ni(II)), 4,4'-bipyridine in the periphery of the elusion droplets coordinated with Ni(II) alternatively resulted in particles entangled with bipyridine–Ni(II) coordination polymer nanowires. After removing organic phase, coils composed of nanowires embedded in polymer matrix were obtained, as shown in Schemes 1 and 2.

The coordination polymer coils were analyzed by using ^1H NMR, FT-IR, UV–vis, and GPC. ^1H NMR spectra of coordination polymer coils in D_2O and $\text{DMSO}-d_6$ are shown in Figure 1. For the purpose of comparison, bipyridine–Ni(II) polymers without EPE were synthesized according to literature protocol.^{33,34} The signals at δ 7.68 and 8.50 attributed to the resonances of pyridine protons of bipyridine–Ni(II) bridge were observed in the ^1H NMR spectrum of the coordination polymer coils in D_2O (Figure 1). This confirmed the formation of bipyridine–Ni(II) bridge in nanowire coils (Scheme 2).^{33,34} In FT-IR spectra (Figure 2), the C=N stretching vibration band of bipyridine shifted from 1595 to 1620 cm^{-1} after coordination with Ni(II).^{33,34} The coordination of 4,4'-bipyridine with Ni(II) was also monitored using UV–vis

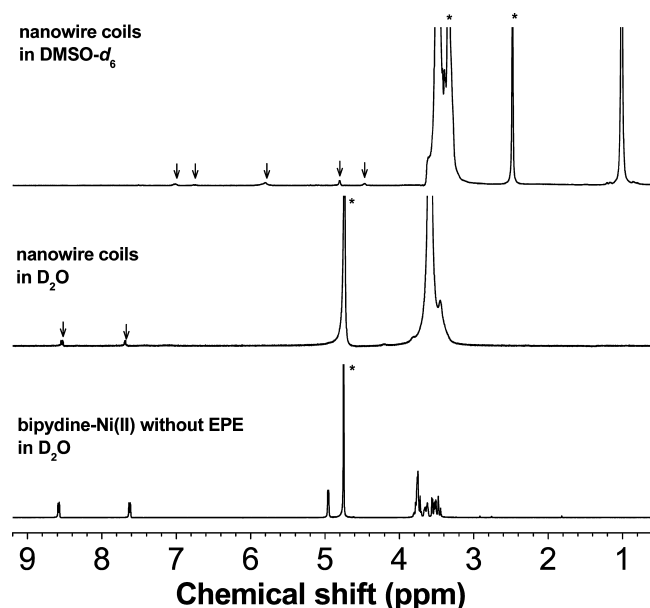


Figure 1. ^1H NMR spectra of nanowire coils and bipyridine–Ni(II) polymers in D_2O and $\text{DMSO}-d_6$. Solvent and water peaks were marked with asterisks.

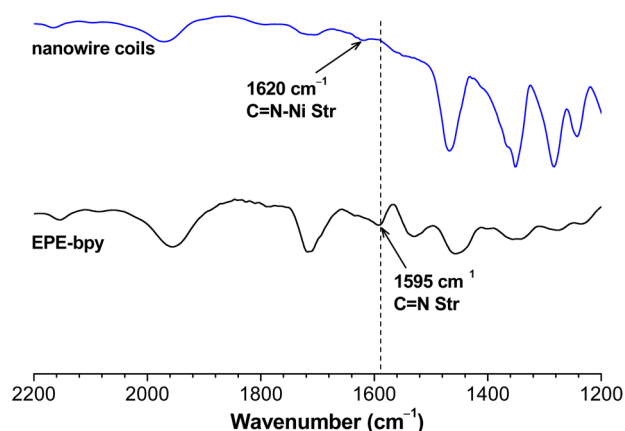


Figure 2. FT-IR spectra of EPE-bpy and nanowire coils.

spectrometry (Figure 3). 4,4'-Bipyridine showed an absorbance band at 243 nm, attributed to $\pi \rightarrow \pi^*$ transition. The absorbance band blue-shifted to 239 nm after coordination with Ni(II). Molecular weight of the coordination polymers was measured by using gel permeation chromatography (GPC). The polymer showed a broad peak at short retention time (Figure 4). The number-average molecular weight of the polymers was 94.2×10^3 g/mol, by far larger than its parent polymer of EPE-bpy (15.5×10^3 g/mol) (Table 1). This revealed the formation of supramolecules by stringing up its parent polymers through Ni(II)/bipyridine coordination polymers (Schemes 1 and 2).

3.2. Morphology of Nanowire Coils. The morphology of the organometallic coordination polymers was characterized using field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), and tapping mode atomic force microscopy (AFM). SEM images showed coil-like particles with size of approximately $2 \mu\text{m}$ (Figure 5). TEM images demonstrated that the coils were composed of thin wires, which were randomly embedded in the polymer matrix. TEM image at high magnitudes revealed that the wires had

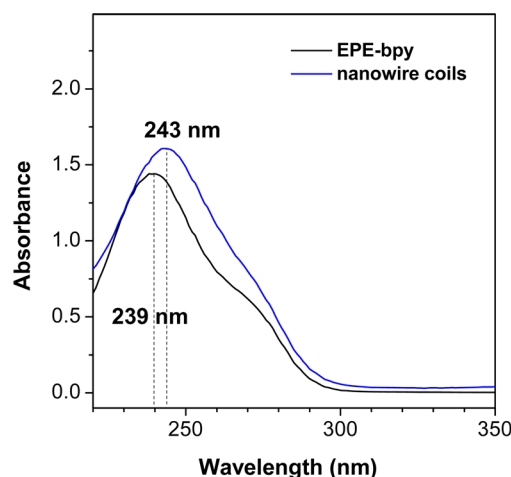


Figure 3. UV-vis spectra of EPE-bpy and nanowire coils. Concentration is 0.1 mg/mL.

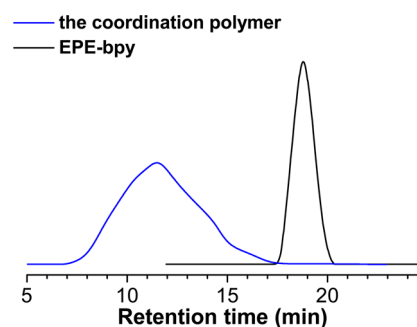


Figure 4. GPC curves of EPE-bpy and the coordination polymer coils.

Table 1. Number-Average Molecular Weight and Polydispersity of EPE-bpy and the Coordination Polymer Coils

sample	M_n ($\times 10^3$ g/mol)	PDI
EPE-bpy	15.5	1.31
coordination polymer	94.2	3.56

diameter of 2 nm and length of tens of nanometers. The AFM image revealed grains with striped surface, further confirming the formation of nanowire coils. The EDX spectrum verified the presence of nickel element in nanowire coils. Nickel weight fraction of nanowire coils was approximately 0.8%.

3.3. Effect of Synthetic Conditions. Because the Ni(II)/bipyridine molar ratio plays a crucial role in the formation of coordination polymers, we investigated the effect of Ni(II)/bipyridine molar ratio on particle morphology (Figure S1, Supporting Information). Irregular aggregates were observed for the emulsion without addition of Ni(II) likely due to disassembly of the emulsion particles during drying. At Ni(II)/bipyridine molar ratio of 1:2, aggregates consisting of small particles were formed. Further increasing Ni(II)/bipyridine molar ratio to 2:1, large irregular aggregates were obtained. At low Ni(II)/bipyridine molar ratio, only small portions of bipyridine coordinated with Ni(II) to form oligomer due to lack of Ni(II), leading to the formation of aggregates consisting of small nanoparticles. While at high Ni(II)/bipyridine molar ratio, oligomer is formed again due to excess of Ni(II). Therefore, optimized Ni(II)/bipyridine molar ratio must exist, where an equivalent molar ratio of Ni(II) and bipyridine

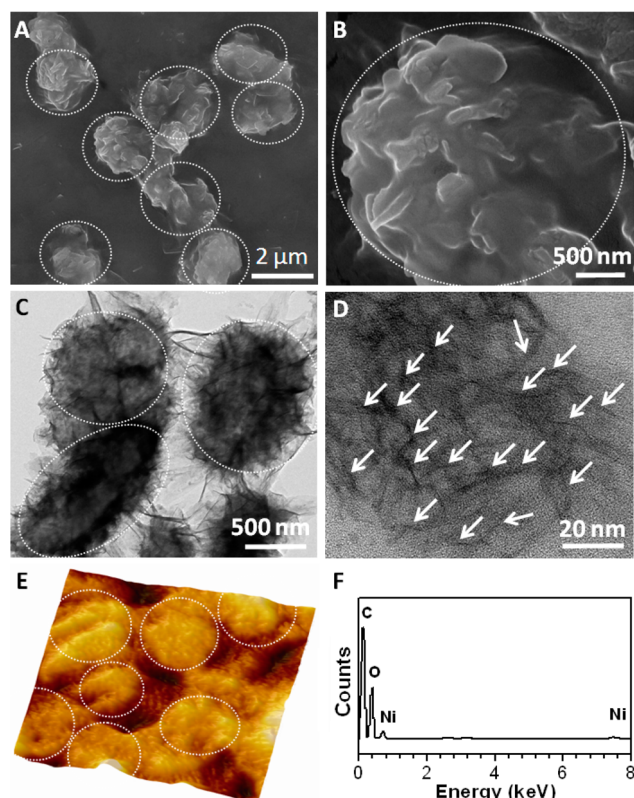


Figure 5. SEM image at low magnification (A) and at high magnification (B), TEM images at low magnification (C) and at high magnification (D), AFM image with size of $5 \times 5 \mu\text{m}^2$ (E), and EDX spectrum (F) of nanowire coils of organometallic coordination polymers. The white dashed-line circles denote nanowire coils.

coordinate alternatively to form coordination polymer chains (Scheme 2). The coordination polymers string up parent polymer of EPE to form supramacromolecules. The rigid Ni(II)/bipyridine coordination polymers prevent emulsion particles from disassembly during removing solvents. Thus, well-shaped coils are retained.

We next investigated the effect of organic phase content on morphology of coordination polymer particles. Without any organic phase, the coordination polymers formed nanoparticles with size of 50 nm (Figure S2, Supporting Information). Coils with diameter of $1 \mu\text{m}$ were observed for the elution with 2.5 wt % organic phase. Containing 10 wt % organic phase in emulsion led to the formation of coils with size of $2.5 \mu\text{m}$. Further increasing organic phase to 20 wt % gave rise to loosely entangled coils with size of approximately $3 \mu\text{m}$.

3.4. Microstructure and Thermal Property. Microstructure of polymer nanowire coils was characterized using X-ray diffractometry (XRD) (Figure 6). Two distinct diffraction peaks, ascribed to (120) and (014) of poly(ethylene oxide) orthorhombic crystals, were observed for nanowire coils. This indicated that poly(ethylene oxide) existed as crystalline structure in nanowire coils.

Thermal stability of nanowire coils was evaluated using thermogravimetric analysis (TGA) (Figure 7). Pristine poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (EPE) began to decompose at 194°C . While nanowire coil began to lose its mass at 367°C , 173°C higher than that of pristine EPE, showing that nanowire coils possessed improved thermal stability contrasting with pristine EPE. A possible

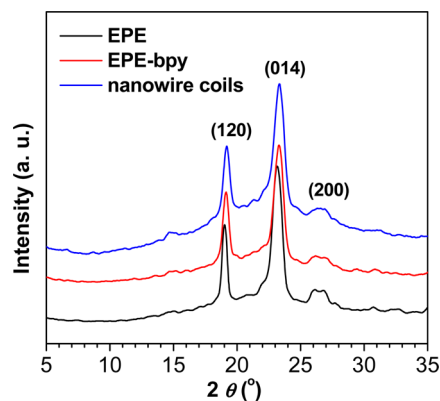


Figure 6. XRD curves of EPE, EPE-bpy, and nanowires coils.

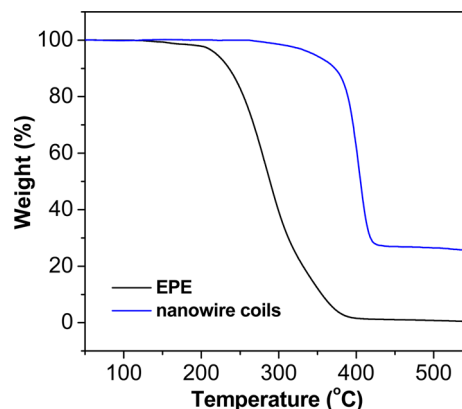


Figure 7. TGA traces of EPE and nanowire coils.

reason is that the coil structure restricts mobility of EPE macromolecules, which prevents the radicals produced during thermal decomposition from propagating.

3.5. Encapsulation and Controlled Release of Cargoes. Nanowire coils possess hydrophobic cavity and hydrophilic periphery entangled with coordination polymer nanowires, which offers a good candidate for encapsulating organic cargoes. We tested the possibility of nanowire coils to encapsulate organic cargo using Nile Red as a model cargo. Loading Nile Red in nanowire coils led to the purple emulsion, which was stable over a week without obvious Nile Red aggregates. When adding hexane into the Nile Red loaded emulsion without stirring and let it stand, the top hexane layer kept clear over 2 days (Figure 8A). This implied that Nile Red molecules were encapsulated by nanowire coils because unencapsulated Nile Red molecules dispersed in aqueous media are not stable. The capability of nanowire coils encapsulating Nile Red is possibly associated with their hydrophobic cavities. Hydrophobic inner walls of the cavities likely prefer to absorb Nile Red molecules via hydrophobic interactions. In contrast, after stirring vigorously and then left standing for 1 h, the purple emulsion layer turned milky because of extraction of Nile Red from nanowire coils by hexane (Figure 8B). The milky aqueous layer implied that polymer nanowire coils retained in aqueous phase after extraction. This is rational since EPE is not soluble in hexane. We therefore used common solvents of dichloromethane (DCM) to extract Nile Red. Nile Red could be readily extracted from nanowire coils by using DCM (Figure 8C), as expected. Interestingly, the aqueous phase remained milky after

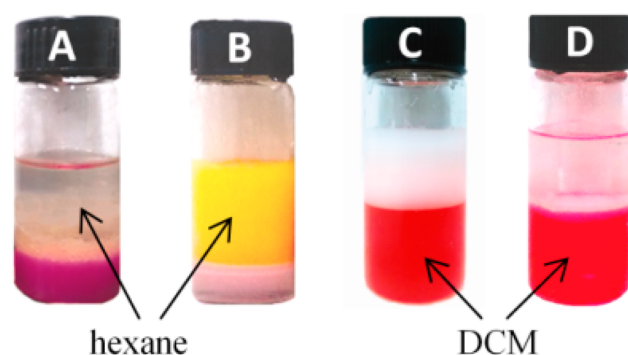


Figure 8. Extraction of Nile Red encapsulated inside nanowire coils: (A) mixing Nile Red loaded nanowire coils with hexane without stirring; (B) extracting Nile Red with hexane; (C) extracting Nile Red with dichloromethane (DCM); (D) extracting Nile Red stabilized with EPE-bpy.

extraction, suggesting that nanowire coils were retained in the aqueous phase. The milky aqueous suspension was centrifuged, and the morphology of the solid was checked using SEM. Again nanowire coils were observed (Figure S3, Supporting Information), verifying that coils remained after extraction. Such selective extraction of nanowire coils is different from their parent polymer of EPE-bpy (Figure 8D) and conventional polymers where capsules were destroyed during extraction.^{36,37} Such selective extraction of cargo of nanowire coils is likely due to the formation of rigid coordination polymer nanowires, which prevents parent polymers from disassembling during extraction, but allowing solvents to penetrate through.

4. CONCLUSIONS

In summary, we synthesized nanowire coils of organometallic coordination polymers by using the emulsion periphery polymerization technique. The nanowire coils were composed of thin wires with diameter of 2 nm. Nanowire coils possessed enhanced thermal stability as contrast to their parent triblock copolymers. Nanowire coils were capable of encapsulating organic cargoes. Encapsulated cargoes could be extracted from nanowire coils without damaging nanowire coils. Nanowire coils are potential candidates for encapsulating and controlled release of organic cargoes.

■ ASSOCIATED CONTENT

Supporting Information

SEM images of particles at various Ni(II)/bipyridine molar ratios and with various organic phase contents; SEM image of nanowire coils after extraction with DCM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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