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β-Cyclodextrin-Capped Polyrotaxanes: One-Pot Facile Synthesis via Click Chemistry and Use as Templates for Platinum Nanowires

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ABSTRACT: Polyrotaxanes (PRs), in which α-cyclodextrins (α-CDs) were threaded onto poly(ethylene glycol) (PEG) chains capped with β-cyclodextrins (β-CDs), were prepared by click chemistry via a one-pot strategy in water at room temperature with high yield, up to 320 mg/100 mg PEG axis. The terminal β-CD cavity could be recognized by phenolphthalein and utilized to form a supramolecular block copolymer with alternate rod and coil segments via the formation of a host−guest inclusion complex with diadamantyl-terminated PEG. The prepared PR could further work as a novel template for the *in situ* deposition of platinum (Pt) nanoparticles (NPs) to fabricate metallic nanowires. TEM and SEM observations showed that the resulting polycrystalline nanowires with length of 50−200 nm and diameter of ca. 12 nm were composed of close-packed uniform Pt NPs with diameter of ca. 2.5 nm. The catalytic activity of the Pt nanowires was demonstrated by the reduction of 4-nitrophenol. The fascinating β-CD-capped PR is promising in a wide variety of fields such as supramolecular chemistry and bionanotechnology due to its facile and salable availability and biocompatibility.

Introduction

Polyrotaxanes (PRs) have attracted great interest over the past decades, especially the one based on α-cyclodextrins (α-CDs) and poly(ethylene glycol) (PEG), which was proposed by Harada et al.[1] in the 1990s for the first time. Until now, a large number of these PRs with different stoppers have been prepared.[2] An efficient method to prepare the PRs in large scale is of particular importance to facilitate further research on these compounds. Most of the reported PRs were prepared via the two-pot strategy, which involved the formation of pseudo-PRs in water and the end-capping reaction in organic solvent (DMF is the most often used solvent).[3] However, due to the dethreading inclination of α-CDs from the axis in DMF, such two-pot strategy might have some negative effects on the yields and the molecular weights of the corresponding PRs. Therefore, a one-pot strategy, which means the end-capping reaction takes place in the aqueous solution of the pseudo-PRs directly, is supposed to be much more efficient. Unfortunately, to date, only a few scientists have tried this strategy. Recently, Arai et al. reported the one-pot synthesis of the PRs via end-capping reaction of diamine-terminated PEG axis with a bulky isocyanate stopper in water at 0 °C.[4,5] Choi et al. utilized a polyethylenimine (PEI)-*b*-PEG-*b*-PEI copolymer as the axis of the pseudo-PR, which could be end-capped by 9-anthraldehyde via the formation of a Schiff-base after lowering the pH of the buffer solution.[6] Besides the α-CD-containing PRs discussed here, Okada et al. also investigated a one-pot method to prepare γ-CD-containing PR by the photocyclodimerization reaction of 9-anthryl groups at the ends of the poly(propylene glycol) axis.[7]

In this article, we developed an alternative one-pot strategy for the preparation of PRs based on α-CDs, as shown in Scheme 1A. "Click" reaction, the Huisgen 1,3-dipolar cycloaddition of azides and alkynes, which was used by Loethen et al.,[8] Zeng et al.,[9] and ourselves[10] to prepare α-CD-based PRs via a two-pot strategy, was chosen as the end-capping reaction here. Compared to most of the reported end-capping reactions, the click reaction has been demonstrated with higher efficiency and tolerance of water,[11] guaranteeing the possibility of a one-pot strategy. Accordingly, a dialkyne-terminated PEG was utilized as the axis of the PR, and more significantly, mono-(6-azido-6-desoxy)-β-cyclodextrin (β-CD−N_3) was chosen as the stopper, giving rise to the terminally recognizable "full-CD" PR. Our one-pot click strategy is demonstrated to bear various significant advantages over the reported ones, such as fast, efficient, green, high yield and high coverage ratio for the resulting biocompatible PR.

β-CD is widely recognized in supramolecular chemistry as a host molecule that is able to include a wide range of guest molecules to form host−guest inclusion complexes.[12] However, the inclusion complexation ability of the terminal β-CD cavities of the PRs has not been properly studied yet.[13] Herein, we found that the terminal β-CD cavity could still be recognized by phenolphthalein to form a colorless inclusion complex in a basic buffer solution.[14] Moreover, the prepared β-CD-capped PR was utilized to form a supramolecular block copolymer with diadamantyl-terminated PEG via inclusion complex linkages.[15] This would open a new avenue for the preparation of supramolecular block copolymers with alternate rod and coil segments.

The efficient accessibility of PRs in large scale promises new explorations for their applications. Many intriguing applications of the PRs have been reported recently, such as slide-ring materials,[16] efficient drug delivery systems,[17] molecular tubes,[18] and so forth.[19] Herein, we tried a brand-new application of the prepared PRs in the field of nanotechnology: use as the template for the *in situ* deposition of platinum (Pt) nanoparticles (NPs) to fabricate nanowire-like nanoclusters. From another point of

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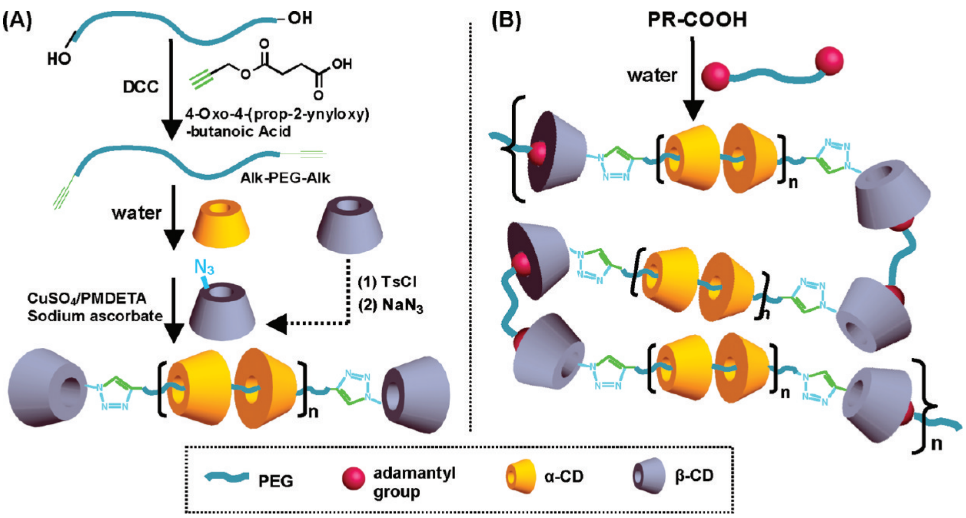
Scheme 1. (A) One-Pot Synthesis of β-CD-Capped PR via Click Chemistry in Water and (B) the Formation of Rod-*b*-coil Supramolecular Copolymers via Host−Guest Inclusion Complexes



view, the Pt NPs could serve as the "indicators", which amplified the small structure of PR and made it discernible under TEM and SEM with high contrast of metal phase over substrate. This unprecedented approach might be developed into a general method for the visualization of soft ultrafine nanostructures with electronic microscopy, which is still regarded as a challenge at present.

Experimental Section

Materials. Poly(ethylene glycol) (PEG) (HO−PEG1−OH, M_n = 4.6 kDa), HO−PEG2−OH (M_n = 12 kDa), HO−PEG3−OH (M_n = 1.5 kDa), (+)-sodium L-ascorbate (98%), 2-adamantanamine hydrochloride (Ada−$NH_2\cdot$HCl, 99%), ethylene glycol (99%), and CuBr (98%, purified according to ref 20 before use) were purchased from Sigma-Aldrich. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, 98%) was purchased from Alfa Aesar. α-Cyclodextrin (α-CD, 99%) and β-CD (99%) were the products of Shaanxi Liquan Chemical Co., Ltd. K_2PtCl_4, dimethyl sulfoxide (DMSO), and all the other materials used were purchased from Sinopharm Chemical Reagent Co., Ltd. Dimethylformamide (DMF) were dried with $MgSO_4$ overnight prior to use. 4-Oxo-4-(prop-2-ynyloxy)butanoic acid was prepared according to the reported procedure in our lab.[21] Mono-(6-*O*-(p-tolylsulfonyl))-β-cyclodextrin (β-CD−OTs) and mono-(6-azido-6-desoxy)-β-cyclodextrin (β-CD−N_3) were synthesized according to ref 22 (^{1}H NMR spectra are shown in the Supporting Information, Figure S2). 4-(2-Azidoethoxy)-4-oxobutanoic acid were prepared according to ref 23. Dialkyne-terminated PEG1 (Alk−PEG1−Alk), dialkyne-terminated PEG2 (Alk−PEG2−Alk), diazido-terminated PEG1 (N_3−PEG1−N_3), alkyne-terminated adamantane (Ada−Alk), and diadamantyl-terminated PEG3 (Ada−PEG3−Ada) were all prepared according to the procedures shown in the Supporting Information.

Instrument. UV−visible spectra were obtained by using a Varian Cary 100 Bio UV−visible spectrophotometer. Gel permeation chromatography (GPC) was recorded on Perkin-Elmer HP 1100 (LiBr/DMF 0.01 mol/L as the eluent, RI-WAT 150CV+ as a detector and polystyrene as a standard at 70 °C). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) measurements were carried out on a Varian Mercury plus 400 NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). Wide-angle X-ray diffraction (WAXD) patterns were obtained by using Rigaku X-ray diffractometer D/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 5.0 deg/min. Atomic force microscopy (AFM) was performed under tapping mode on a NanoScope IIIa SPM from Digital instruments Inc. The AFM samples were prepared via spin-coating method to form monolayer of PR on a freshly peeled mica wafer. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope at 200 kV. Scanning electron microscopy (SEM) images were recorded using Hitachi S-4800 field-emission microscope. Dynamic light scattering (DLS) was measured on a Brookhaven 90 Plus particle size analyzer.

Synthesis of PR with Alk−PEG1−Alk via One-Pot Strategy (PR1A). A typical synthetic procedure of PR1A is depicted as follow. At room temperature, a mixture of Alk−PEG1−Alk (100.0 mg, 0.04 mmol CH≡C−) and α-CD (1.00 g, 1.03 mmol) in water (10 mL) was ultrasonically agitated for 5 min and then stirred overnight to form pseudo-PR1A. To this mixture, β-CD−N_3 (187.9 mg, 0.16 mmol, the molar ratio of β-CD−N_3 to CH≡C− was 4:1), $CuSO_4\cdot 5H_2O$ (40.5 mg, 0.16 mmol), PMDETA (34.5 μL, 0.16 mmol) and (+)-sodium L-ascorbate (64.2 mg, 0.32 mmol) were added subsequently under nitrogen atmosphere and the reaction was then carried out at room temperature for 2 h in the darkness. After centrifugation, the precipitate was dissolved in DMSO and reprecipitated in deionized water. This purification cycle was repeated twice. The precipitate was washed with hot water (50 °C) several times and then dried under vacuum at 65 °C for 24 h to get a white powder. Yield: 320 mg/100 mg PEG axis. ^{1}H NMR (DMSO-d_6, δ, ppm): 3.22−3.43 (br overlapped, H-2,4), 3.51 (CH_2 of PEG), 3.52−3.84 (br overlapped, H-3,5,6), 4.46 (m, OH-6), 4.78 (m, H-1), 5.41−5.51 (m, OH-2,3).

The hydroxyl groups of PR can be converted into other functional moieties for application purposes. We prepared carboxylated (PR1A−COOH) and valeryl chloride-modified PR1A (PR1A−VC) according to protocols reported in refs 24 and 25, respectively (see Supporting Information).

Synthesis of PR with Alk−PEG1−Alk via Two-Pot Strategy (PR1B). The synthesis of pseudo-PR1B was similar to that reported in ref 26. At room temperature, a mixture of Alk−PEG1−Alk (100.0 mg, 0.04 mmol CH≡C−) and α-CD (1.00 g, 1.03 mmol) in water (10 mL) was ultrasonically agitated for 5 min and then stirred overnight. The resulting white precipitate was collected by filtration and then washed with deionized water several times to remove the unthreaded α-CDs. The precipitate was dried under vacuum at 65 °C for 2 d to get the white pseudo-PR1B (Yield: 0.67 g). To a 25 mL Schlenk flask containing 4 mL of DMF were added subsequently β-CD−N_3 (0.60 g, 0.52 mmol −N_3), CuBr (49.5 mg, 0.34 mmol), PMDETA (74 μL, 0.34 mmol) and 0.60 g pseudo-PR1B powder under nitrogen atmosphere, and the reaction was carried out at 0 °C overnight. The reaction mixture was then poured into deionized water. The precipitate was collected by centrifugation and the purification procedure of the crude product was the same as that of the one-pot strategy. Yield: 156 mg/100 mg PEG axis. ^{1}H NMR spectrum of PR1B in DMSO-d_6 was similar to that of PR1A (Supporting Information, Figure S3A).

Synthesis of PR with N_3-PEG1$-N_3$ via Two-Pot Strategy (PR1C). The synthesis and purification procedures for PR1C were similar to those of PR1B, except that N_3-PEG1$-N_3$ (100.0 mg) was used instead to prepare the pseudo-PR1C and Ada$-$Alk was utilized as the end-capping reagent. The product was further purified by precipitating in acetone to remove the residual end-capping agent. The yield of pseudo-PR1C was 0.63 g and that of PR1C was 89 mg/100 mg PEG axis. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.67$-$1.97 (m, H of adamantyl group), 3.20$-$3.41 (br overlapped, H-2,4), 3.51 (CH_2 of PEG), 3.57$-$3.81 (br overlapped, H-3,5,6), 4.27 (m, OH-6), 4.79 (m, H-1), 5.30$-$5.40 (m, OH-2,3) (Supporting Information, Figure S4A).

Preparation of Pt NPs with the Template of PR1A$-$COOH. The as-prepared PR1A$-$COOH (30 mg) and deionized water (6 mL) were placed into a 50 mL Schlenk flask. Then four drops of 1 M NaOH solution and 9 mL of ethylene glycol were added. Under magnetic stirring, K_2PtCl_4 (19.2 mg, 0.046 mmol) in 5 mL of ethylene glycol/deionized water solution (3:2 volume ratio) was added. The mixture was heated in a 125 °C oil bath under nitrogen atmosphere for 4 h. After cooling to room temperature, the product was precipitated in acetone, separated by centrifugation, and stored in water to give a brown solution. Part of the solution was centrifuged and dried under vacuum at 60 °C overnight to afford a black solid.

Results and Discussion

Synthesis and Characterization of PR1A. The detailed synthetic route for PR1A is depicted in Scheme 1A. The axes of PR1A were prepared via the facile DCC/DMAP condensation between HO$-$PEG1$-$OH and 4-oxo-4-(prop-2-ynyloxy)butanoic acid, and then the as-prepared axes were mixed with α-CDs to form the white pseudo-PR1A in aqueous solution. As to the end-capping reagent, β-CD was treated with p-toluenesulfonyl chloride (TsCl) first to prepare β-CD$-$OTs, which then reacted with NaN_3 to give rise to the novel stopper, β-CD$-N_3$. We considered β-CD$-N_3$ as the stopper because: (1) the size of β-CD (maximum external and minimum internal diameters are 1.5 and 0.6 nm, respectively) is exactly suitable to prevent α-CD (maximum external and minimum internal diameters are 1.4 and 0.45 nm, respectively) from dethreading; (2) it is water-soluble and biocompatible; (3) it can be prepared in large scale cost-effectively; (4) the stopper and the wheel have the same functional groups ($-$OH) and similar chemical properties, which are quite important in the further modifications and applications of PRs; and (5) the resultant PRs could be further assembled into supramolecles via the host$-$guest inclusion complexes between the terminal β-CD moieties and guest molecules. The stoppers were then added to the aqueous solution of the pseudo-PR1A to yield PR1A via the Cu(I)-catalyzed "click" reaction of azides and alkynes. It is known that click reaction has many intrinsic merits, such as fast and standardized procedure, wideness in scope, high yields, no byproducts, and the most important one to the end-capping reaction, tolerance of water.[27] Hence, click chemistry has been widely used as a versatile method for the preparations of functional monomers,[28] functional polymers,[29] bioconjugated polymers,[30] dendritic copolymers,[31] etc. In this article, click chemistry was employed for the first time as the fast end-capping reaction in the one-pot synthesis of PR. The resulting PR1A was dissolved in DMSO, precipitated in water, and carefully washed with hot water. After the strict repeated purification steps, the yield decreased from 600$-$700 mg to 320 mg/100 mg PEG axis as a result of the elimination of unthreaded PEG axes, free α-CDs, residual β-CD$-N_3$, low molecular weight of PRs, and the catalyst, giving rise to a white powder finally.

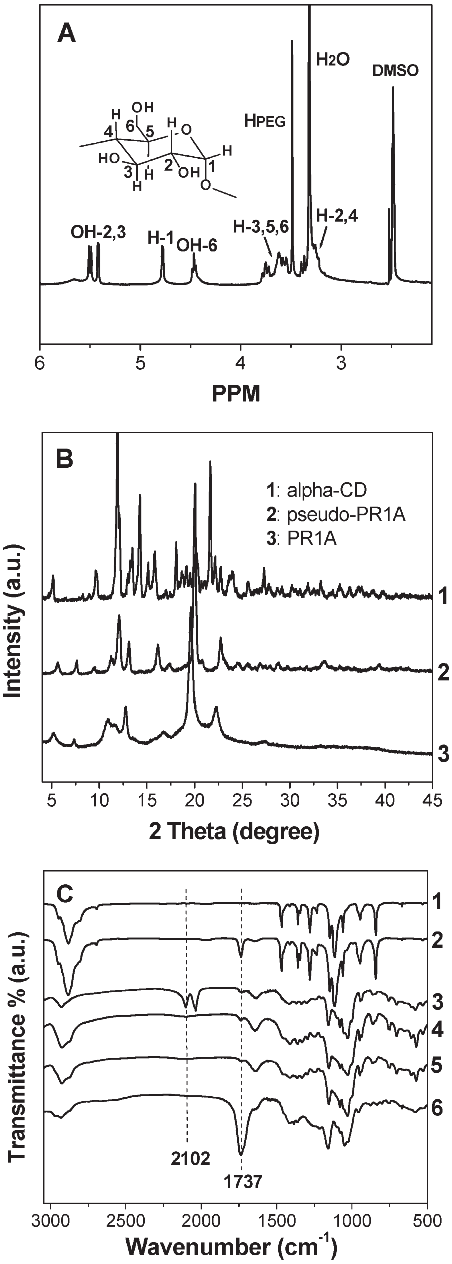


Figure 1. (A) ^{1}H NMR spectrum of PR1A in DMSO-d_6. (B) WAXD patterns of (1) α-CD, (2) pseudo-PR1A, and (3) PR1A. (C) FTIR spectra of (1) HO$-$PEG1$-$OH, (2) Alk$-$PEG1$-$Alk, (3) β-CD$-N_3$, (4) pseudo-PR1A, (5) PR1A, and (6) PR1A$-$COOH.

The structure of PR1A was characterized and confirmed by ^{1}H NMR, WAXD, and FTIR. The ^{1}H NMR spectrum of PR1A is shown in Figure 1A. The proton peak at 3.49 ppm is assigned to the hydrogen atoms of the PEG axis and all of the other peaks belong to the protons from two kinds of CD rings. The number of the threaded α-CDs per axis (N_{CD}) can be calculated from the integration values of PEG peak and H-1 peak of CD at 4.78 ppm. The value of N_{CD} is ca. 32.9 and the corresponding coverage ratio, which is calculated from the ratio of N_{CD} to the theoretical maximum amount of α-CDs threaded by the axis,[5] equals ca. 63%. As shown in

Table 1. Reaction Conditions and Results for the Preparation of β-CD-Capped PRs

sample[a]	R[b]	reaction time (h)[c]	yield (mg/100 mg PEG axis)	M_n (kDa)[d]	PDI[f]	N_{CD} (ca.)[g]	coverage ratio (%)[j]
PR1A	1	8	160	102	1.22	37.1[h]	70
	1.2	8	240	e			
	2	8	300				
	4	8	310	100	1.24	36.4[h]	69
	8	8	280				
	4	0.17	250	90.8	1.32	33.1[h]	63
	4	0.5	230				
	4	1	280				
	4	2	320			32.9[i]	63
PR1B	13	overnight	156			27.4[i]	52
PR2A	4	2	75	120	1.48	41.6[h]	31

[a] In sample code "PR*n*X", "*n*" represents M_n of PEG axis, 4.6 (1) or 12 (2) kDa and "X" denotes the synthetic strategy, one-pot (A) or two-pot (B). [b] The molar feed ratio of β-CD$-$N$_3$ to alkyne unit. [c] Reaction time of click end-capping reaction. [d] M_n of corresponding valeryl chloride-modified PR obtained from GPC. [e] The data are not available. [f] GPC polydispersity index. [g] The number of the threaded α-CDs per axis. [h] The values are gotten via GPC method. [i] The value is based on ^{1}H NMR. [j] The ratio of N_{CD} to the theoretical maximum amount of α-CDs threaded by the axis.

Figure 1B, the WAXD patterns of pseudo-PR1A and PR1A show strong and sharp diffraction peaks at $2\theta = 20°$, manifesting the existence of channel-type α-CD inclusion complexes in these two compounds.[32] The synthetic procedure of PR1A can be also followed by FTIR spectra, as shown in Figure 1C. After esterification of HO$-$PEG1$-$OH with 4-oxo-4-(prop-2-ynyloxy)butanoic acid, the characteristic peak of carbonyl is clearly observed at 1737 cm^{-1}. This peak can still be found in the FTIR spectra of pseudo-PR1A and PR1A, but with decreased intensity; while in that of PR1A$-$COOH, it increases significantly due to the increase of carbonyl concentration. In addition, the absorption peak of azide associated with β-CD$-$N$_3$ at 2102 cm^{-1} disappears in the FTIR spectrum of PR1A, revealing that the residual end-capping reagent has been removed entirely from the final product.

To optimize the click end-capping, we investigated the effects of reaction time and the amount of the end-capping reagent on the yield of PR1A. The results are listed in Table 1. As a consequence, in the whole tested range, the maximum yield, 320 mg/100 mg PEG axis, was achieved when the molar feed ratio of β-CD$-$N$_3$ to alkyne unit (R) was 4 and the end-capping reaction time was 2 h. The yield is comparable to or better than those published before.[2,4−7] The extremely short reaction time is a prominent advantage of this one-pot strategy. Previously, it always needed tens of hours or even a few days to accomplish an end-capping reaction. On the contrary, in our case, the yield could approach as high as 250 mg/100 mg PEG axis when R was 4, approximate 78% of the maximum value, while the end-capping reaction was carried out for only 10 min. Such a high yield in such a short time confirmed the high efficiency of the one-pot click synthetic strategy. It is noteworthy that even in the case of lower R (e.g., $R = 1$), a yield of 160 mg/100 mg PEG was achieved with prolonged reaction time (8 h). This indicated that relatively high yield could also be attained with very economic amount of end-capping reagent via one-pot strategy, mainly owing to the fact that pseudo-PR1As can exist stably for a long time in the presence of free α-CDs dissolved in the aqueous solution.

It is worth mentioning that PR1As synthesized under different conditions of end-capping reaction have the same molecular weights or N_{CD}s despite different yields. The three typical kinds of PR1As were first treated with valeryl chloride to improve their solubility in organic solvent in order to perform GPC measurements with the common DMF eluent. We found that the number-average molecular weights (M_n) of the resultant PR1A$-$VCs were almost the same, ca. 100 kDa (Table 1 and Supporting Information, Figure S5). This phenomenon can be explained by the fact that the dynamic equilibrium between threading and dethreading of α-CDs on a linear PEG axis exists in the aqueous mixture of pseudo-PR1As and free α-CDs,[33] which keeps the number of α-CDs per pseudo-PR1A molecule unaltered during the end-capping reaction. Additionally, the coverage ratio resulting from GPC is ca. 69%, which is in agreement with the value obtained via NMR method. In comparison with the reported coverage ratio (ca. 51−66%) of the PR consisting of PEG with similar M_n (4 kDa) prepared via two-pot strategy,[34] the results gotten via one-pot method herein are superior.

In order to further compare the two strategies discussed in this article, such full-CD PRs were synthesized via a conventional two-pot strategy as well. The yield of resulting PR1B is only 156 mg/100 mg PEG axis and the value of N_{CD} obtained from the ^{1}H NMR spectrum (Supporting Information, Figure S3A) is ca. 27.4 with coverage ratio of ca. 52%. The obviously lower values of yield and N_{CD} could be attributed to (1) the extra isolation process of pseudo-PR1B from water and (2) the strong dethreading inclination of α-CDs from the axis in DMF since no additional free α-CDs could be employed to restrain the partial dissociation of pseudo-PR1B during the end-capping reaction. Therefore, there is no doubt that the one-pot strategy excels the two-pot one greatly in terms of process, efficiency, yield, coverage ratio, reproducibility, etc.

Moreover, the one-pot strategy is a general method to prepare PRs with different PEG axis. The as-prepared PR2A (M_n of the PEG axis is 12 kDa, yield: 75 mg/100 mg PEG axis) was also characterized and confirmed by ^{1}H NMR, FTIR, WAXD, and GPC, as shown in Figure S6 (Supporting Information). ^{1}H NMR spectrum of PR2A was similar to that of PR1A, except that the intensity of PEG peak increased significantly. The values of N_{CD} and coverage ratio are ca. 44.5 and ca. 33%, respectively, according to the ^{1}H NMR spectrum and the values obtained via GPC are ca. 41.6 and ca. 31%, respectively. The lower coverage ratio should be ascribed to the much higher molecular weight of PEG axis, i.e., the longer axis always resulting in the lower coverage ratio.[35] Nevertheless, the coverage ratio of PR2A possessing longer PEG axis ($> 30\%$) is quite comparable to that of similar PRs prepared via the two-pot strategy.[36]

AFM Observation of PR1A. How to observe PR molecules clearly via microscopy still poses a big challenge. Up until now, scanning tunneling microscopy (STM) is the only well-developed method to characterize the linear structures of PRs[37] and to observe the single CD molecule of the supramolecular complexes.[38] Atomic force microscopy (AFM) is another powerful and novel tool not only for the visualization

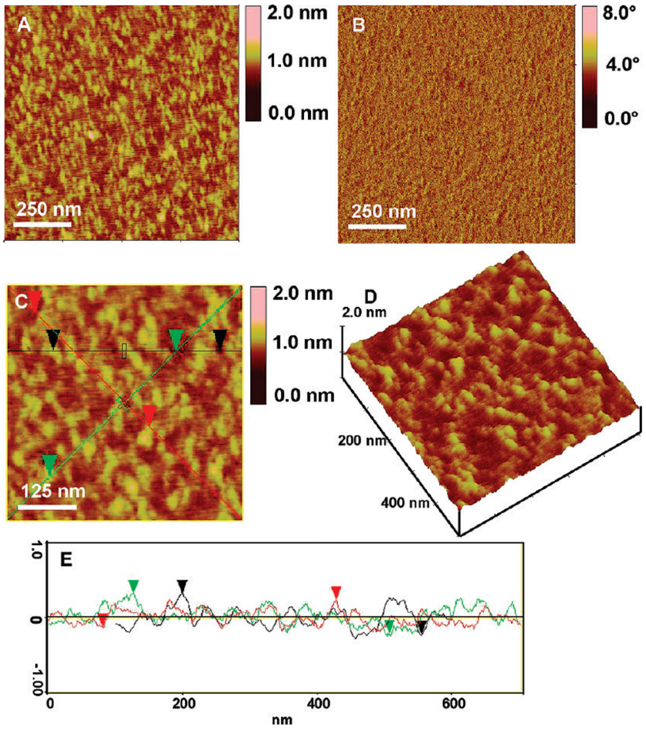


Figure 2. Height (A, C), phase (B) and 3D (D) AFM images of PR1A on a mica wafer (4×10^{-3} mg/mL). (E) section analysis of image C.

of molecules but also for the manipulation and actuation of the microstructures.[39] However, so far, few scientists have utilized AFM to observe the microstructures of PRs after the pioneer reports by Loethen et al.[8] and Cacialli et al.[40]

In this work, tapping mode AFM imaging was conducted to reveal the microstructures of the prepared PRs. As shown in Figure 2, a worm-like topology is clearly observed in both height and phase AFM images. According to the surface plot (Figure 2E), the average height of the peaks is 0.53 nm, which is smaller than the anticipated diameter of single PR1A molecule (ca. 1.4 nm). This phenomenon might be caused by the slightly flattened conformation of α-CD on a substrate and the exposure of the partially threaded thin PEG axis to the probe during AFM analysis. The obtained average height is supposed to be the numerical average of α-CD and PEG diameters according to ref 41. Wide-field image of PR1A (Figure 2A) shows that the lengths of part of the observed features are ~30 nm, being in good agreement with the anticipated length of PR1A, ca. 26.3 nm (the length of each α-CD is 0.8 nm[42] and the value of N_{CD} is ca. 32.9 according to the NMR method). Larger structures with lengths ranging from 50 to 100 nm and widths from 10 to 15 nm are observed as well, which are likely attributed to the remarkable alignment and aggregation of β-CD-capped PR1As via hydrogen bonds. In addition, since the AFM probe normally offers a typical tip radius of ca. 10 nm, it is hard to get high resolution images for a target less than 1 nm, especially for the soft matter. Additional AFM images are shown in Supporting Information, Figure S7. Apparently, compared to STM, the AFM images exhibited lower resolution and more research is needed to improve this method in the future.

Terminal Supramolecular Recognition. The β-CD-capped PR1A is expected to act as a host molecule to form supramolecular complexes with guest molecules including phenolphthalein and diadamantyl-terminated PEG.

As shown in Figure 3A, upon the addition of 43 equiv of β-CD$-$N$_3$ (6 mg, 5 μmol), the characteristic UV$-$visible

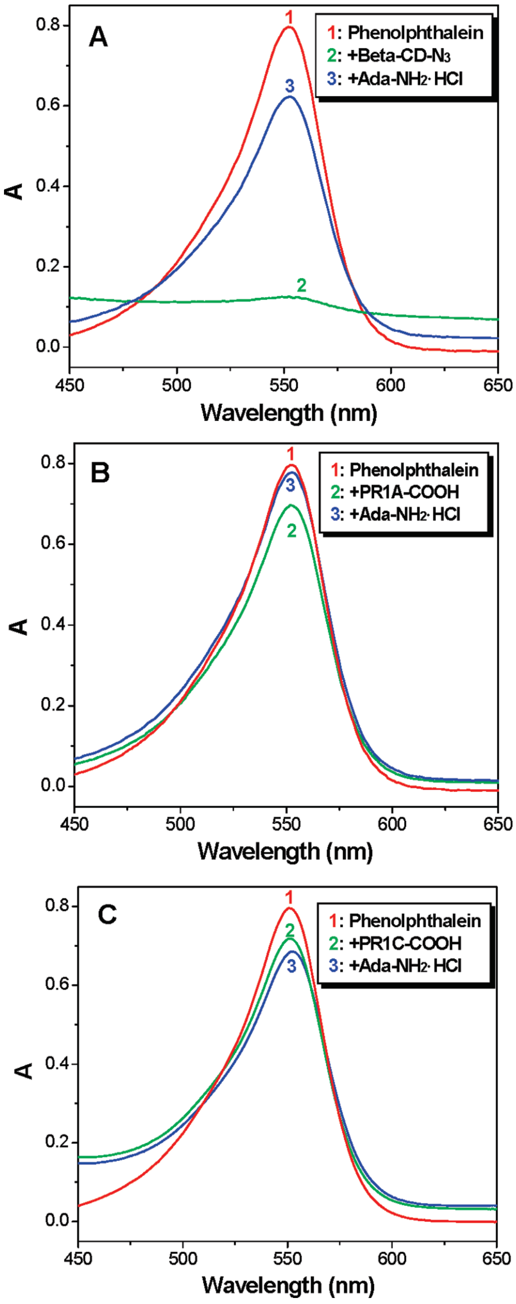


Figure 3. Effects of β-CD$-$N$_3$ (A), PR1A$-$COOH (B), and PR1C$-$COOH (C) addition to the UV$-$visible spectra of a 30 μM phenolphthalein solution (pH = 10.5 HCO_3^-/CO_3^{2-} buffer solution, 4 mL): (1) dye only, (2) dye and 6 mg of β-CD$-$N$_3$ (or PR$-$COOH), and (3) dye, 6 mg of β-CD$-$N$_3$ (or PR$-$COOH), and 2 mg of Ada$-$NH$_2\cdot$HCl.

absorption at ca. 552 nm of a 30 μM phenolphthalein solution (pH = 10.5 HCO_3^-/CO_3^{2-} buffer solution, 4 mL, 0.12 μmol phenolphthalein) decreases from 0.80 to 0.13 due to the formation of the colorless inclusion complex between the indicator and β-CD cavity. Part of the included indicator was then substituted by the added Ada$-$NH$_2\cdot$HCl (2 mg, 0.01 mmol), which binds more strongly to β-CD, resulting in the recovery of absorption to 0.62. Likewise, this phenomenon can be utilized to demonstrate the complexation ability of the terminal β-CD moieties of PR1A. PR1A was first treated with succinic anhydride to improve its solubility in the buffer solution. The mixture solution was stirred at room temperature for 4 d in a sealed flask after the addition of each

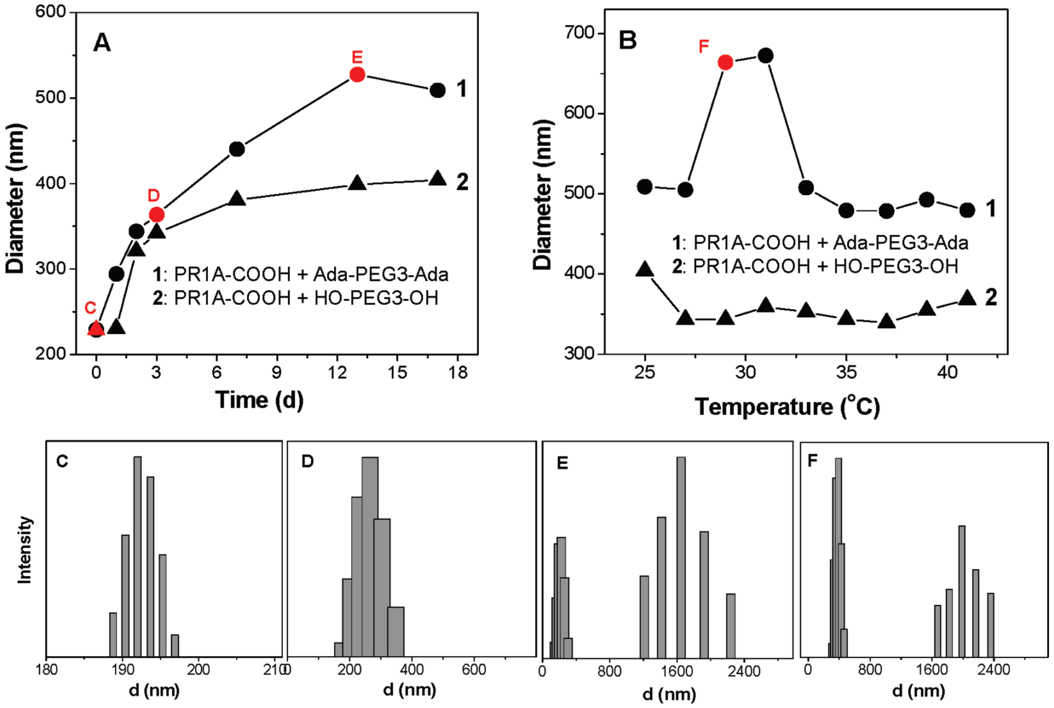


Figure 4. Effects of stirring time (A) and temperature (B) on the formation of supramolecular copolymers consisting of PR1A−COOH and Ada−PEG3−Ada followed by DLS: (1) the sample composed of 10 mg of PR1A−COOH, 0.2 mg of Ada−PEG3−Ada, 4 mL of water, and 0.2 mL of pH = 10.5 HCO_3^-/CO_3^{2-} buffer solution and (2) a control experiment (Ada−PEG3−Ada was substituted by HO−PEG3−OH). The multimodal size distribution results of the red plots in parts A and B are shown in parts C−F.

compound. In the presence of PR1A−COOH (6 mg, 0.1 μmol β-CD moieties), the characteristic absorption at ca. 552 nm decreased from 0.80 to 0.70 owing to the complexation of terminal β-CD cavities with phenolphthalein, and then recovered to 0.78 due to the partial substitution of Ada−NH_2·HCl (Figure 3B). In contrast, when PR1A−COOH was changed to PR1C−COOH that was capped with adamantly groups in the control experiment, the intensity of the absorption peak keeps decreasing after each addition (Figure 3C). Therefore, we can draw the conclusion that the terminal β-CD moiety of PR1A still retained the complexation ability with the corresponding guest molecules.

The formation of β-CD/adamantane inclusion complexes is highly favorable with an association constant of 10^4 M^{-1} in water because of the good fit of the adamantyl group inside the β-CD cavity.[43] Therefore, adamantyl containing and β-CD-containing molecules are widely employed as the building blocks in the field of supramolecular chemistry to prepare linear or dendritic supramolecular copolymers, noncovalent cross-linked gel, polymeric micelles, etc.[44] Hasegawa et al. once prepared a “coil-*b*-coil” supramolecular copolymer via the inclusion complex between the PEG bridged β-CD dimers and the adamantyl guest dimers.[45] However, according to our knowledge, the supramolecular copolymer with alternate rod and coil segments, “rod-*b*-coil” copolymer, has never been reported yet. Herein, β-CD capped PRs were utilized as the rod building blocks to form supramolecular copolymers with diadamantyl-terminated PEG in aqueous solution (Scheme 1B) and the whole process was followed by DLS.

The tested sample was composed of 10 mg of PR1A−COOH (0.2 μmol β-CD moiety), 0.2 mg of Ada−PEG3−Ada (0.2 μmol adamantyl group), 4 mL of water, and 0.2 mL of pH = 10.5 HCO_3^-/CO_3^{2-} buffer solution. As shown in Figure 4A, the diameter of the particle sizes of the sample increases gradually from 229.0 to 509.1 nm when stirred at room temperature for 17 d. By comparison, in the control experiment (Ada−PEG3−Ada was substituted by HO−PEG3−OH), the diameter of the mixture merely rises to 404.0 nm likely due to the significant aggregation of the components via hydrogen bonds in the present of PEG chain since no obvious increase of diameter was observed in PR1A−COOH solution without the addition of PEG. Therefore, the extra increase of the diameter, ca. 105.1 nm, should be attributed to the existence of supramolecular copolymer in the aqueous solution. Additionally, as shown in Figure 4B, the diameter of the sample increases from 509.1 to 664.0 nm with increasing temperature to 29 °C, indicating the formation of more β-CD/adamantane complex linkages. When the temperature rises to 33 °C, part of the linkages dissociated, causing the decrease of diameter to ca. 500 nm. This decomplexation behavior is supposed to be driven by the entropy gain upon dissociation of the mobile Ada−PEG3−Ada molecules.[46] However, in the temperature range of 35−41 °C, due to the relatively high mobility of the inclusion complex itself, the entropy driving force becomes much weaker, so part of the complex linkages remains and the diameter changes little. As a comparison, in the control experiment, within the same investigated temperature range, the diameter of the mixture decreases slightly due to the partially dissociation of the aggregates when heated. Furthermore, particles with larger sizes, ca. 2000 nm, were also found in the tested sample (Figure 4C−F), which is another evidence for the formation of supramolecular copolymers. However, DLS can hardly give the exact sizes of the rod-like supramolecular copolymers and we are trying to work out a resolution now.

In addition to the DLS measurements, tapping mode AFM was also utilized to reveal the different morphologies of these two aforementioned comparable samples, as shown in Figure 5. In the presence of Ada−PEG3−Ada, the microstructures of the tested sample (with average length and width of ca. 82 and ca. 13 nm, respectively) were

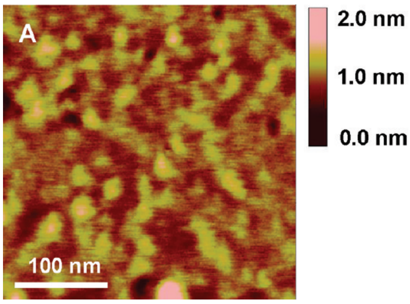


Figure 5. Height AFM images of (A) the sample composed of 10 mg of PR1A−COOH, 0.2 mg of Ada−PEG3−Ada, 4 mL of water, and 0.2 mL of pH = 10.5 HCO_3^-/CO_3^{2-} buffer solution, and (B) the sample for control experiment (Ada−PEG3−Ada was substituted by HO−PEG3−OH) on mica wafers. Both the samples were diluted with water and the concentration of PR1A−COOH was ca. 4×10^{-3} mg/mL.

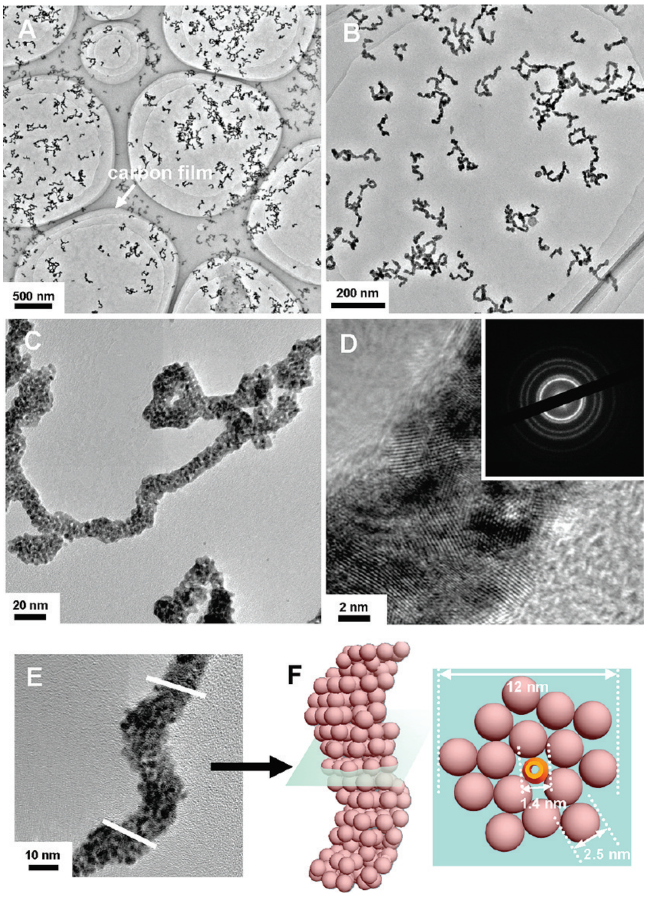


Figure 6. TEM images (A−E) and simulated cartoon (F) of the nanowires of Pt nanoclusters based on PR1A−COOH. The inset in part D shows the electron diffraction pattern of the sample.

obviously larger than those of the sample for control experiment (with average length and width of ca. 26 and ca. 8 nm, respectively), also indicating the formation of the rod-*b*-coil copolymers. Because of the complexicity of the supramolecular copolymer, nevertheless, to know the exact block numbers is still an open question.

Supramolecular Template for Pt NPs. The electron microscopes such as TEM and SEM are powerful and versatile tools for the characterization of nanostructures. However, most of the ultrafine organic nanostructures cannot be observed directly by TEM or SEM because of their low phase contrast and decomposition under high energy. Then, is it possible to characterize the PR chains by TEM or SEM in an indirect way? We speculated that this goal could be possibly realized by the *in situ* growth of metal NPs on the PR chains to form organic/inorganic hybrid nanowires. Nanowire is an intensively studied one-dimensional (1D) nanostructure,[47] and polymer brushes,[48] organic surfactants,[49] DNA,[50] peptide nucleic acid (PNA),[51] etc. have been used as the templates of metal nanowires, but the use of a supramolecular PR has never been tried. Herein, we prepared Pt nanowires with Pt NPs evenly deposited *in situ* along the PR chains, and accordingly, the nanostructures were amplified and high contrast TEM and SEM images were obtained. Pt was chosen as the model metal to prepare nanowires in terms of the potential application of the nanowires in catalysis.

In the presence of PR1A−COOH, K_2PtCl_4 was reduced *in situ* in a solution of ethylene glycol and water, affording the colloidal Pt NPs, which were suspended stably in water resulting in a brown liquid. The resultant aqueous sample was loaded onto a copper grid and observed by TEM, and highly dispersive nanowires were clearly found (Figure 6 and additional images are shown in Supporting Information, Figure S8). Figure 6F shows the simulated 3D cartoon and 2D cross-section image of a nanowire section. Each polycrystalline nanowire of Pt nanocluster is composed of close-packed Pt NPs with uniform size of ca. 2.5 nm and the average width of the nanowire is ca. 12 nm. The lengths of the observed nanowires are in the range of 50−200 nm, much longer than single PR1A (only ~30 nm). This phenomenon is likely ascribed to the following: (1) the stretched PR1A−COOH chain with the attached rigid Pt NPs; (2) the linkage of two close PRs by one Pt NP; (3) the hydrogen bonds between the two terminal β-CD moieties, which elongated the templates in aqueous solution; and (4) the entanglement of the resulting Pt nanowires.

SEM was also employed to characterize the structure of the sample and similar morphology was observed, as shown in Figure 7. Furthermore, energy dispersive X-ray spectroscopy (EDS) analyses indicated that the Pt content in the sample is as high as ca. 93.9 wt % (Figure 8A). WAXD pattern of the Pt nanoclusters (Figure 8B) shows three peaks at 2θ = 40.0, 46.4, and 68.0°, which are assigned to the diffractions from (111), (200), and (220) planes of face-centered cubic (fcc) Pt crystals, respectively.[52] The average diameter of individual Pt NP was ca. 2.3 nm calculated using the Debye−Scherrer formula from the Pt (111) diffraction peak, which is coincident with the electron microscopy observation.

The catalytic activity of the prepared Pt nanoclusters was demonstrated via the reduction of 4-nitrophenol, which can be reduced to 4-aminophenol in the presence of sodium borohyride and catalyst.[53] After the addition of a trace amount of the as-prepared Pt nanoclusters, the characteristic UV−visible absorption peak of 4-nitrophenol at 400 nm quickly decreased with the concomitant appearance of the peak of 4-aminophenol at 310 nm (Figure 9). The catalytic

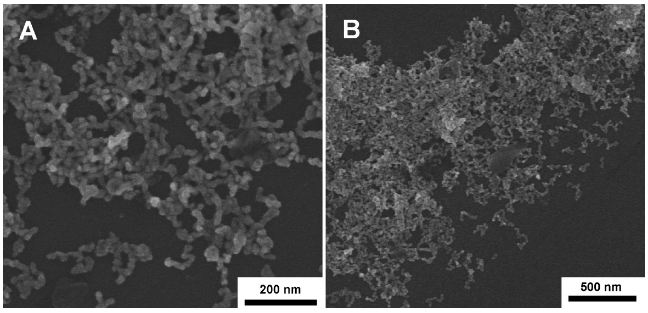


Figure 7. SEM images of the nanowires of Pt nanoclusters based on PR1A−COOH on silicon surface.

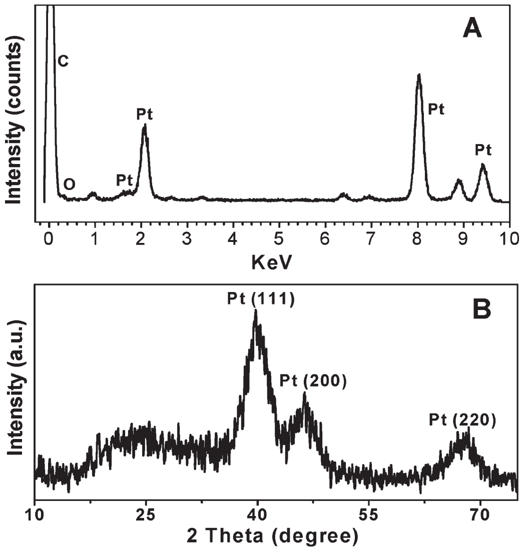


Figure 8. (A) EDS spectrum and (B) WAXD pattern of Pt nanoclusters based on PR1A−COOH.

activity is assumed to result from the high density and high surface area of the Pt NPs that decorated on the surface of the template. We believe that the PR can be used as a general template for the fabrication of nanowires of various metals and inorganic compounds, opening the new direction of nanowires of polycrystalline nanoclusters. Work on these details is in progress and will be reported later.

Conclusions

In summary, we have developed a facile one-pot synthetic strategy for the PR made from α-CDs, dialkyne-terminated PEG, and β-CD−N_3 end-capping reagent in aqueous solution at room temperature via azide−alkyne "click" reaction. This promising strategy shows the following advantages: (1) the synthetic procedures are simplified; (2) the process is green and environmentally friendly since almost all compounds included are biocompatible and the reaction is carried out in water; (3) the resultant PRs are prepared controllably with high yield and high coverage ratio; and (4) the terminal β-CD cavities can be recognized by phenolphthalein and adamantyl group, opening a new way for the preparation of novel rod-*b*-coil supramolecular copolymers. Moreover, after treatment with succinic anhydride, the PR could be utilized as a novel template for the *in situ* deposition of Pt NPs and the polycrystalline nanowires of Pt nanoclusters were observed via TEM and SEM with high contrast. The application possibility of the Pt nanowire as a catalyst was also investigated and the catalytic activity for the reduction of 4-nitrophenol was revealed. The provision of facile one-pot synthetic route combined with the revolutionary application of PRs as supramolecular templates would not only facilitate the preparation of PR but also highlight the great potential of PR as a precursor of various intriguing functional materials.

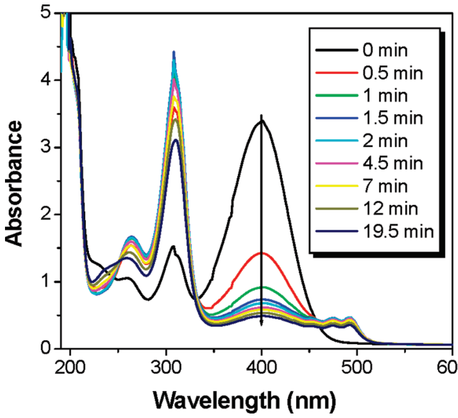


Figure 9. Successive UV−visible spectra of the mixture of 4-nitrophenol and Pt nanoclusters upon addition of sodium borohydride. [4-nitrophenol]$_0$ = 0.2 mmol dm^{-3}, [$NaBH_4$]$_0$ = 10 mmol dm^{-3}.

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Supporting Information Available: Text giving experimental details and figures showing chemical structures of the compounds, ^{1}H NMR spectra of β-CD−OTs and β-CD−N_3 in DMSO-d_6, GPC traces of the three typical kinds of PR1A−VCs, characterization of PR1B, PR2A, and PR1C, and additional AFM images of PR1A; additional TEM images of Pt nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.

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