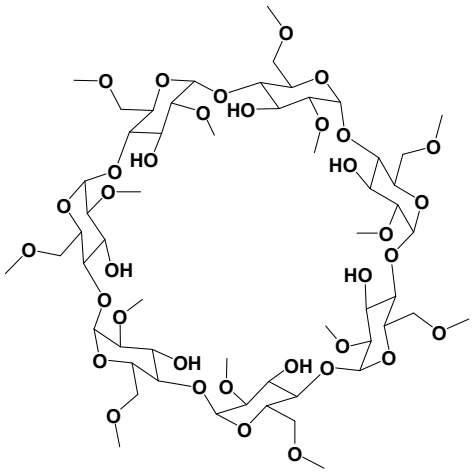
Supporting Information

1. Experimental Section

1.1 Materials.

α-Cyclodextrin (α-CD) was purchased from Sigma and dried under high vacuum at 100 °C for 24 h before use. (*R,S*)-β-butyrolactone (> 95 %, Tokyo Kasei Inc) was dried over and vacuum distilled from CaH_2 twice before use. Poly(ethylene glycol) methyl ether (MPEG) with M_n of ca. 2000 Da was obtained from Aldrich. MPEG was first purified by dissolving in dichloromethane followed by precipitation into diethyl ether and further dried under high vacuum at 60 °C for 24 h before use. Doxorubicin hydrochloride (DOX, Apollo Scientific), 2-Bromopropionic bromide (97 %, Aldrich), sodium azide (NaN_3, ≥ 99.5 %, Sigma-Aldrich), 1-adamantaneacetic acid (98 %, Aldrich), propargyl bromide solution (80 wt.% in toluene, Aldrich), propargylamine (98 %, Aldrich), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 98 %, Sigma-Aldrich), sodium ascorbate (≥ 99 %, Aldrich), heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD, ≥ 98.0 %, Aldrich) (structure shown in scheme S1), Fluorescein 5(6)-isothiocyanate (FITC, ≥ 90 %, Fluka), N,N-dimethylacetamide (DMAc, anhydrous, 99 %, Aldrich), dimethylformamide (DMF, > 99 %, Tedia), methylene chloride (CH_2Cl_2, 99 %, Tedia) tetrahydrofuran (THF, > 99 %, Tedia), diethyl ether (Et_2O, 99 %, Tedia) and *n*-hexane (95 %, Tedia) were used as received.



Scheme S1. Chemical structure of heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD).

1.2 Synthesis of bromine-functionalized star α-CD-core (CD-s-Br).

The bromine-functionalized star α-CD-core was synthesized following a similar method to previous reports.[1] α-CD (2.43 g, 2.5 mmol) was dissolved in 30 mL of anhydrous DMAc with stirring and cooled to 0 °C. Subsequently, a solution of 2-bromopropionic bromide (10.8 g, 50 mmol) in anhydrous DMAc (20 mL) was added dropwise to the α-CD solution for a period of 1 h at 0 °C under N_2 atmosphere. After stirring at room temperature for 2 days, the reaction mixture was precipitated with 1 L of n-hexane. The resulting powder was collected by centrifugation and redissolved in CH_2Cl_2 (80 mL), then the solution was successively washed with 1 M HCl (aq) solution, saturated $NaHCO_3$ (aq) solution, 1 M NaCl (aq) solution, and water. The organic phase was dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator after filtration. The residues were further purified by silica gel column chromatography using THF as eluent and dried under vacuum. Yield: 6.2 g (73.4 %, based on substitution degree of 18). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (m, -CH(C<u>H</u>$_3$)Br), 3.55-6.00 (m, protons of α-CD and –C<u>H</u>(CH$_3$)Br); ^{13}C NMR (100 MHz, $CDCl_3$): 170.0 (C=O), 96.2 (C-2, C-3 of α-CD), 66.7-75.1 (C-1, C-4, C-5 of α-CD), 64.4 (C-6 of α-CD), 39.9 (-<u>C</u>H(CH$_3$)Br), 21.6 (-CH(<u>C</u>H$_3$)Br).

1.3 Synthesis of azide-functionalized star α-CD-core (CD-s- N_3).

CD-s-Br (0.83 g, 4 mmol) was dissolved in 10 mL DMF, 1.30 g of NaN_3 (20 mmol) was added. After stirring at 60 °C for 2 days, the reaction mixture was precipitated with 200 mL of water. The resulting powder was collected by centrifugation, washed with water. The residues were further purified with Sephadex LH-20 using THF as eluent and dried under vacuum. Yield: 0.58 g (85.3 %, based on substitution degree of 13). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (m, -CH(C<u>H</u>$_3$)N_3), 3.12-5.97 (m, protons of α-CD and –C<u>H</u>(CH_3)N_3); ^{13}C NMR (100 MHz, $CDCl_3$): 170.7 (C=O), 94.7-105.0 (C-2, C-3 of α-CD), 67.9-75.1 (C-1, C-4, C-5 of α-CD), 63.9 (C-6 of α-CD), 57.8 (-<u>C</u>H(CH_3)N_3), 17.0 (-CH(<u>C</u>H_3)N_3).

1.4 Synthesis of α-Adamantyl-ω-alkynyl-poly(3-hydroxybutyrate (PHB).

The heterofunctionalised PHB was synthesized via anionic ring-opening polymerization of (*R*,*S*)-β-butyrolactone in DMSO at room temperature under dry N_2 atmosphere, similar to the method reported previously.[2] The initiator sodium adamantaneacetate (Ada-CH_2CO_2Na) was obtained from the neutralization of commercially available adamantaneacetic acid with sodium hydroxide in methanol. In a typical example, the ring opening polymerization was initiated by reacting 0.63 g of dried Ada-CH_2CO_2Na (2.9 mmol) with 2.38 mL of β-butyrolactone monomer (30 mmol) in 80 mL of anhydrous DMSO at room temperature. With the aid of ^{1}H NMR monitoring, the polymerization was quenched by adding an excess of propargyl bromide upon reaching a monomer conversion of >90 %. Solvent DMSO was then removed by rotary evaporation and the crude polymer sample was re-dissolved in chloroform, filtered and precipitated into n-hexane to afford the purified polymer. Yield: 2.5 g (82.2 %, based on theoretical yield computed using actual monomer conversion). GPC (THF): M_n = 0.89 kDa, PDI = 1.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26-1.31 (m, -OCH(C<u>H</u>$_3$)CH_2CO_2- of

PHB), 1.59-1.71 (m, methylene protons of adamantyl end group), 1.95 (br, methine protons of adamantyl end group), 2.02 (s, -OCC$\underline{H}_2$-Ada) 2.43-2.62 (m, -OCH(CH_3)C$\underline{H}_2CO_2$- of PHB and –$OCH_2C{\equiv}C\underline{H}$ of alkynyl end group), 4.68 (s, -OC$\underline{H}_2C{\equiv}CH$), 5.23-5.32 (m, -OC$\underline{H}$($CH_3$)$CH_2CO_2$- of PHB). ^{13}C NMR (100 MHz, $CDCl_3$): 169.6-172.2 (-$\underline{C}$O- of PHB and -$\underline{C}OCH_2$-Ada), 75.5 (alkynyl group), 67.9 (-$\underline{C}$H- of PHB), 52.4 (-$\underline{C}H_2$-alkynyl), 49.3 (-$\underline{C}H_2$-adamantyl), 41.1 (-$\underline{C}H_2$- of PHB), 42.7, 37.0, 33.1, 28.9 (adamantyl group), 20.1 (-$\underline{C}H_3$ of PHB).

1.5 Synthesis of α-CD-core star polymer (CD-s-PHB-Ada) via alkyne-azide coupling.

CD-s-PHB-Ada was synthesized via alkyne-azide coupling in DMSO/H_2O system. In a typical example, a bottle with an N_2 inlet was charged with 1.01 g of PHB (M_n (EA) 1.01 kDa, 1 mmol), 0.22 g of CD-s-N_3 (M_n (^{1}H NMR and EA) 2.23 kDa, 0.1 mmol) and 2 mL DMSO. A freshly prepared 23 wt% aqueous solution of $CuSO_4{\cdot}5H_2O$ (0.3 mmol) and 33 wt% aqueous solution of sodium ascorbate (0.63 mmol) were then added sequentially. The reaction was allowed to stir at room temperature under N_2 atmosphere for 2 days. The reaction mixture was diluted with THF and passed through alumina column to remove copper residue. Then, the polymer solution was precipitated into Et_2O. The product was collected by filtration and purified twice by dissolution / precipitation with THF / Et_2O, and dried under vacuum overnight. Yield: 0.90 g (73.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00-1.55 (m, -OCH(C$\underline{H}_3$)CH_2CO_2- of PHB and -CH(C$\underline{H}_3$)N-), 1.55-1.76 (m, methylene protons of adamantyl end group), 1.94 (br, methine protons of adamantyl end group), 2.01 (s, -OCC$\underline{H}_2$-Ada), 2.35-2.85 (m, -OCH(CH_3)C$\underline{H}_2CO_2$- of PHB), 3.20-5.90 (m, -OC$\underline{H}$(CH_3)CH_2CO_2- of PHB and protons of α-CD), 7.73-8.03 (s, -C=C$\underline{H}$-N- of triazole). ^{13}C NMR (100 MHz, $CDCl_3$): 165.4-172.8 (-$\underline{C}$O- of PHB and -$\underline{C}OCH_2$-Ada and -O$\underline{C}$O-CHCH_3N-), 143.0 (-CH=$\underline{C}$- of triazole), 124.0 (-$\underline{C}$H=C- of triazole), 48.4-68.0 (-$\underline{C}$H- of PHB and carbons of α-CD), 41.2

(-$\underline{C}H_2$- of PHB), 42.7, 37.1, 33.2, 29.0 (adamantyl group), 20.2 (-$\underline{C}H_3$ of PHB), 17.0 (-CH($\underline{C}H_3$)N-).

1.6 Synthesis of fluorescein-labeled CD-s-PHB-Ada (CD-s-PHB-Ada-FITC).

CD-s-PHB-Ada-FITC was synthesized via alkyne-azide coupling reaction of **CD-s-N_3**, heterofunctionalised PHB and FITC-alkyne. FITC-alkyne was synthesized by reacting FITC with propargylamine in anhydrous DMSO at room temperature under the dark for 48 h. The obtained FITC-alkyne was mixed with PHB and CD-s-N_3 in DMSO. A freshly prepared 23 wt% aqueous solution of $CuSO_4 \cdot 5H_2O$ and 33 wt% aqueous solution of sodium were then added sequentially. The alkyne-azide coupling reaction was allowed to proceed for 2 days to produce CD-s-PHB-Ada-FITC.

1.7 Synthesis of CD-s-PHB-MPEG.

The synthesis method for CD-s-PHB-MPEG is nearly the same as that for CD-s-PHB-Ada but using different initiator in PHB synthesis. The synthetic routes of the initiator (MPEG-PHB-alkyne) and the final product (CD-s-PHB-MPEG) were shown in Figure S5. For the synthesis of CD-s-PHB-MPEG, MPEG-COONa was used as macroinitiator to produce MPEG-PHB with alkynyl functionality, and finally obtain CD-s-PHB-MPEG. The macroinitiator endowed with sodium carboxylate functionality on the end of MPEG chain was synthesized through two steps as reported previously,[2] including a TEMPO-mediated oxidation of commercially available hydroxyl-terminated PEG and subsequent neutralization with Na_2CO_3.

1.8 Preparation of inclusion complexes.

To prepare the inclusion complexes, 900 μl of DI water was added into 100 μl of the mixture of CD-s-PHB-Ada (4 mg/mL) and DM-β-CD (various concentrations) in DMF. All the final solutions had the same CD-s-PHB-Ada concentration of 0.4 mg/mL, and the concentration of DM-β-CD depended on the desired weight ratio of CD-s-PHB-Ada to DM-β-CD. The volume ratio of water to DMF is 9/1 in the final solution.

1.9 Measurements and characterization methods

Molecular characterization. Gel permeation chromatography (GPC) measurements were done at 40 °C on a Shimadzu SIL-10A and LC-20AD system equipped with two Phenogel 5μ 100 and 10^4 Å columns (size: 300 × 4.6 mm) connected in series and a Shimadzu RID-10A refractive index detector. THF was used as the mobile phase at a flow rate of 0.3 mL/min. Monodispersed PEG standards were used to calibrate the system. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker Avance DRX 400 MHz NMR spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm with reference to solvent peak ($CHCl_3$: δ 7.26 ppm for ^{1}H NMR and δ 77.2 ppm for ^{13}C NMR). Fourier transform infrared (FTIR) spectra of polymers in KBr were recorded on a Perkin-Elmer FTIR 2000 spectrometer in the region of 4000-500 cm^{-1}. Elemental analyses (EA) were carried out using a Perkin-Elmer 2400 CHN/CHNS elemental analyzer.

Dynamic light scattering measurements. The size of aggregates was measured on a Zetasizer Nano ZS (Malvern Instruments Ltd., MA, USA), with a laser light wavelength of 633 nm at a 173° scattering angle. The particle size measurements were performed at 25 °C in duplicate.

Microscopy. Transmission electron microscopy (TEM) images were taken on a Philips CM300 FEG TEM, operating at 300kV. TEM sample was prepared by two steps. First, a drop of sample solution was placed onto a 200 mesh carbon coated copper grid and left for 2

min before excess liquid was removed by filter paper. Then 1.5 μL of phosphotungstic acid (PTA, 1 wt%) was deposited onto the grid and left for 30 seconds before excess liquid was removed by filter paper. The sample was kept in a dry box for 48 h at room temperature before TEM imaging. Atomic force microscopy (AFM) samples were prepared by casting a drop of sample solution on silica substrate and dried at room temperature for 48 h in a dry box. AFM imaging was done on a multimode-Digital Instrument using the tapping mode with setting of 512 pixels/line and 1 Hz scan rate. NANOSENSOR PPP-NCHR POINTPROBE Silicon-SPM-Probe, silicon cantilever for non-contact-/ tapping-mode was used for the measurement. The images were flattened and analyzed by cross-sectional study.

1.10 Intracellular drug release and cytotoxicity assays

Preparation of DOX-loaded nanovesicles. To prepare the DOX-loaded nanovesicles, 900 μl of water (pH=3) was added into 100 μl of the mixture of CD-s-PHB-Ada-FITC (4 mg/mL), DM-β-CD (80 mg/mL) and DOX (0.67 mg/mL) in DMF. To encapsulate DOX by pH gradient method and remove DMF, the mixture was dialyzed against water (pH=7) overnight using dialysis tube (MWCO 500). The solution was then transferred to dialysis tube (MWCO 1000) and dialysis was continued for a further 3 h to remove unencapsulated free DOX. The concentration of DOX loaded into nanovesicles was determined by measuring UV absorbance at 485 nm.

***In vitro* cytotoxicity test.** For each well in a 96-well plate, 100 μL of Hela cells in DMEM, with a concentration of 1×10^5 cells/mL, was added. The number of Hela cells in each well was 10000. After incubation for 24 h in incubator (37 °C, 5 % CO_2), the culture medium was changed to 100 μL of DMEM containing DOX-loaded nanovesicles or free DOX with various concentrations and the mixture was further incubated for 24 h. Then, DMEM with materials was replaced by fresh DMEM and 10 μL of MTT solution (5 mg/mL)

was added to the cells. After incubation for 4 h, 150 μL of DMSO was added and shaken at room temperature. The optical density (OD) was measured at 570 nm with a microplate reader (Spectra Plus, TECAN). The viable rate was calculated by the following equation:

$$\text{Viable rate} = (OD_{treated} / OD_{control}) \times 100\ \%$$

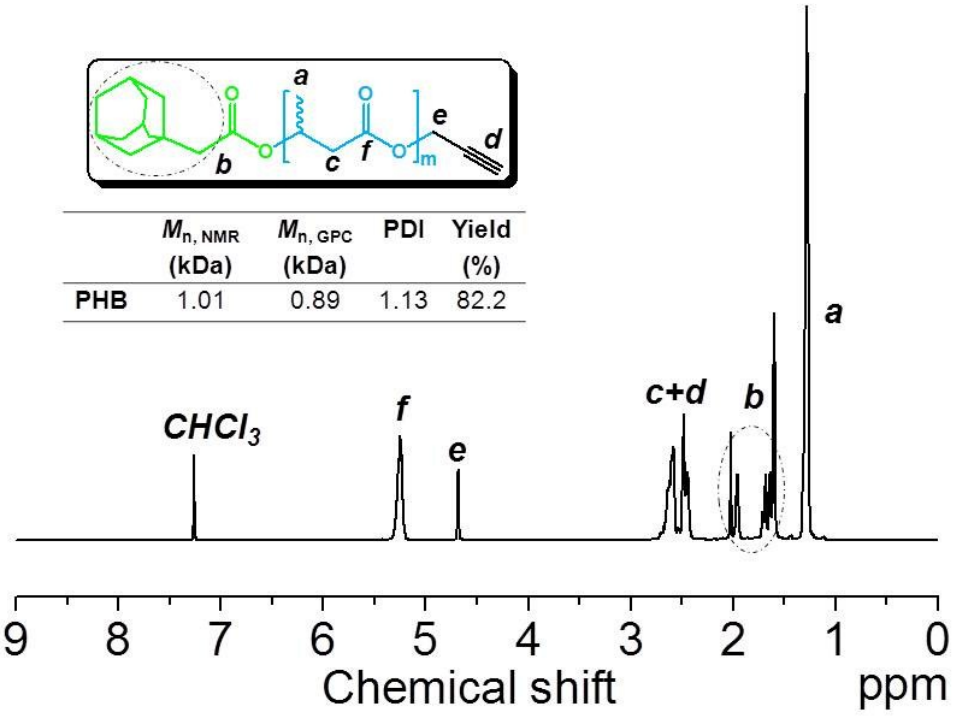
Where, $OD_{control}$ was obtained in the absence of materials and $OD_{treated}$ was obtained in the presence of materials.

Evaluation of cellular uptake. For cell uptake study, Hela cells were cultured on lab-Tek 8-chambered coverglass (Nalge-Nane international, USA) at density of 1.5×10^4 cells/well in 300 μL of complete DMEM with 5 % CO_2 at 37 °C. After 24 h incubation, DOX-loaded nanovesicles or free DOX diluted in the medium at a concentration of 4 μg/mL were added into the chamber. Cells were washed thrice with PBS after incubation for 1 h, 2 h, 4 h and 8 h. The cells were then fixed by 200 μL of 4 % paraformaldehyde (PFA) solution in PBS for 30 min. The cell were washed thrice with PBS and observed by confocal laser scanning microscope (CLSM) (Fluoview FV1000, Olympus, Japan). FITC and DOX were excited by the 488 nm laser and emissions for FITC and DOX were collected at 515-545 and 565-605 nm, respectively.

2. Molecular characteristics of CD-s-PHB-Ada and its precursors

Heterofunctionalized PHB, with telechelic adamantyl moiety and alkynyl functionality, was synthesized in a one pot fashion by anionic ring opening polymerization (ROP) of racemic β-butyrolactone. The ROP procedure proceeded with excellent control over the molecular weight, molecular weight distribution and end-group fidelity (Scheme 1). This has allowed facile incorporation of heterofunctionality, through a judicious selection of anionic initiator and nucleophilic capping agent, onto a PHB precursor with desired molecular weight. Adamantaneacetate and propargyl bromide were chosen as the initiator and capping agent,

respectively, to produce PHB that is able to participate in CD-binding as well as alkyne-azide conjugation. The degree of polymerization (DP) and M_n of PHB were evaluated from ^{1}H NMR spectrum (Figure S1) based on the intensity ratio of PHB methine proton at around δ 5.2 ppm to alkynyl end group protons at around δ 4.7 ppm. DP and M_n were estimated to be 9 and 1.01 kDa, respectively. In addition, both alkynyl and adamantyl end groups of the PHB polymers are clearly identified in ^{1}H NMR spectrum. Together with the relatively narrow PDI as determined from GPC, all of the above characterization data attest to the well-defined nature of the heterofunctionalized PHB.



	$M_{n,NMR}$ (kDa)	$M_{n,GPC}$ (kDa)	PDI	Yield (%)
PHB	1.01	0.89	1.13	82.2

Figure S1. ^{1}H NMR spectrum of heterofunctionalized PHB in $CDCl_3$ with corresponding peak assignments. Alkynyl and adamantyl end groups can be clearly seen in the spectrum. The close agreement of M_ns as determined from NMR and GPC as well as the narrow PDI of molecular weight confirm the well-defined nature of the two PHB polymers synthesized.

The successful syntheses of all the macromolecules were demonstrated by ^{13}C NMR as shown in Figure S2. ^{1}H NMR was used to elucidate the chemical structure of the obtained

CD-s-PHB-Ada copolymer, as shown in Figure S3. All signals in the spectrum can be ascribed to protons belonging to either PHB, α-CD, linkage group or end group. The appearance of signal assigned to triazole proton can be clearly seen at δ 7.8~8.0 ppm. GPC measurement on the star-block copolymer gave narrow molecular weight distribution (PDI=1.07), which indicates that the alkyne-azide coupling proceeded well to give uniform star-block copolymers. The M_n and arm number of the star-block copolymer were evaluated to be 9.28 kDa and 7.0, respectively, based on the nitrogen content and the molecular weight of CD-s-N_3 from elemental analyses (EA) measurements.

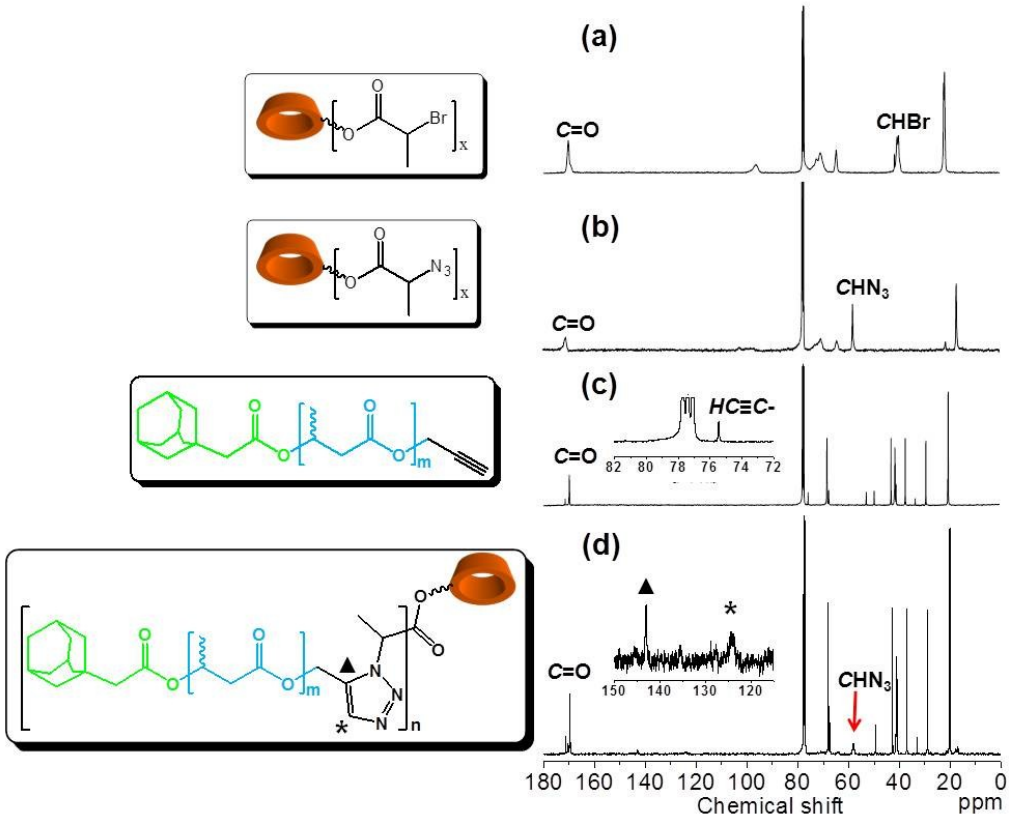
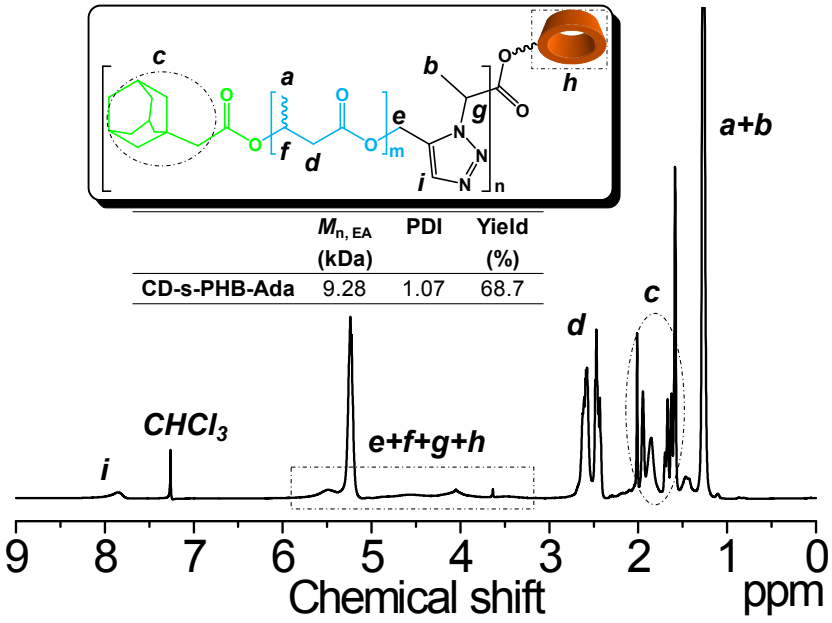


Figure S2. ^{13}C NMR spectra of (a) CD-s-Br, (b) CD-s-N_3, (c) PHB, and (d) CD-s-PHB-Ada in $CDCl_3$.



	$M_{n,EA}$ (kDa)	PDI	Yield (%)
CD-s-PHB-Ada	9.28	1.07	68.7

Figure S3. ^{1}H NMR spectrum of CD-s-PHB-Ada in $CDCl_3$ with corresponding peak assignments. Triazole linking group and adamantyl end group can be clearly seen in the spectrum.

The successful alkyne-azide coupling was also confirmed by comparing the FTIR spectra of CD-s-Br, CD-s-N_3, PHB, and CD-s-PHB-Ada, as shown in Figure S4. The presence of azide end-group of CD-s-N_3 was confirmed by the characteristic azide signal at 2112 cm^{-1}. After coupling reaction, the azide peak decreased a lot in the spectrum of CD-s-PHB-Ada. It should be noted that not all azide groups of CD-s-N_3 were reacted, which have been demonstrated by ^{13}C NMR and FTIR spectra. These results correspond well with the estimation of 7 arms of CD-s-PHB-Ada and 13 azide groups of CD-s-N_3.

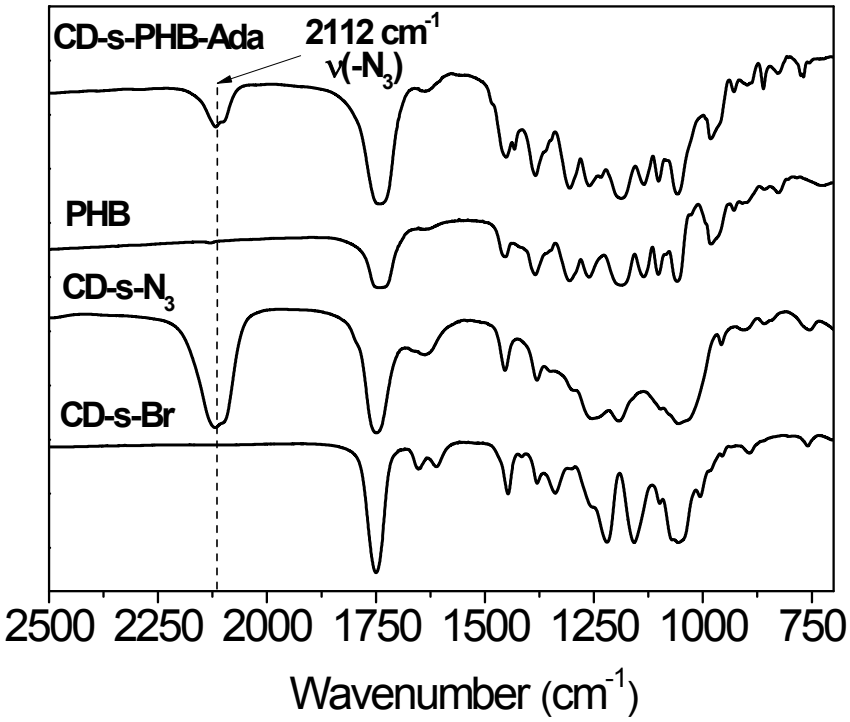


Figure S4. FTIR spectra of CD-s-PHB-Ada and its precursors in the form of KBr discs.

3. Synthesis and characterization of CD-s-PHB-MPEG

In order to observe the self-assembly properties of CD-s-PHB-Ada, the control polymer, CD-s-PHB-MPEG was synthesized. The synthesis method was nearly the same as that for CD-s-PHB-Ada but using different initiator in PHB synthesis. The synthetic routes of the final product (CD-s-PHB-MPEG) and the macroinitiator (MPEG-PHB-alkyne) were shown in Figure S5. For the synthesis of CD-s-PHB-MPEG, MPEG-COONa was used as initiator to produce MPEG-PHB with alkynyl functionality, and finally led to CD-s-PHB-MPEG.

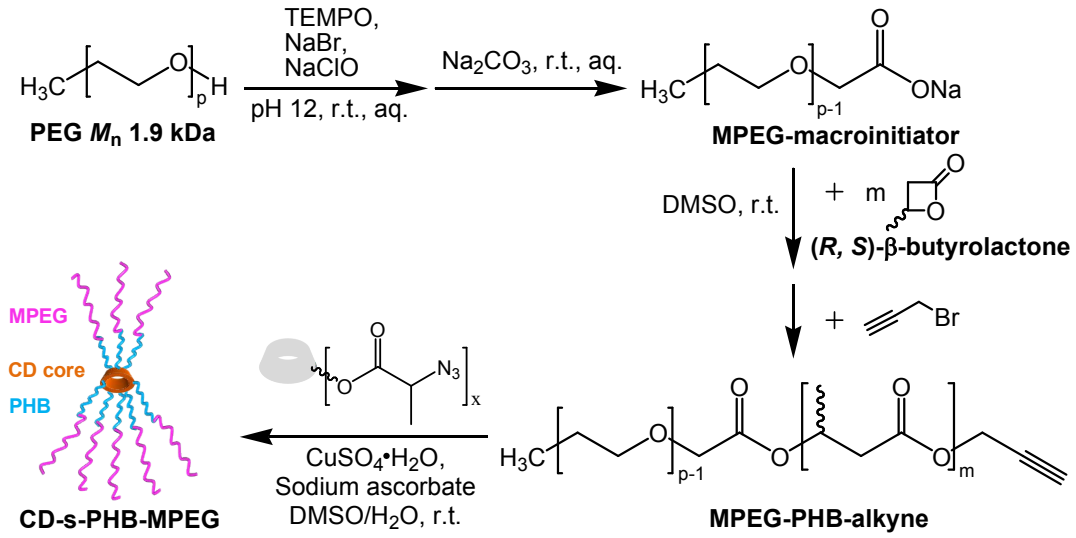


Figure S5. Synthetic route of CD-s-PHB-MPEG and the macroinitiator, MPEG-PHB with alkynyl functionality (MPEG-PHB-alkyne).

The chemical structures of CD-s-PHB-MPEG and its precusor were investigated by ^{1}H NMR, as shown in Figure S6. The degree of polymerization (DP) and M_n of PHB were evaluated from ^{1}H NMR spectrum based on the intensity ratio of PHB methine proton at around δ 5.2 ppm to alkynyl end group protons at around δ 4.7 ppm. The DP of PHB and M_n of PHB-MPEG were evaluated from ^{1}H NMR spectrum to be around 9 and 2.69 kDa, respectively. The alkynyl end group of the PHB is clearly identified in ^{1}H NMR spectrum. Together with the relatively narrow PDI as determined from GPC, all of the above characterization data attest to the well-defined nature of the macroinitiator. All signals in the ^{1}H NMR spectra of CD-s-PHB-MPEG can be ascribed to protons belonging to either PHB, α-CD, linkage group or end group. The appearance of signal assigned to triazole proton can be clearly seen at δ 7.8~8.0 ppm. The M_n of the star-block copolymer was evaluated to be 22.43 kDa and the arm number was further calculated to be 7.5, based on the nitrogen content and the molecular weight of CD-s-N_3 from elemental analyses (EA) measurements.

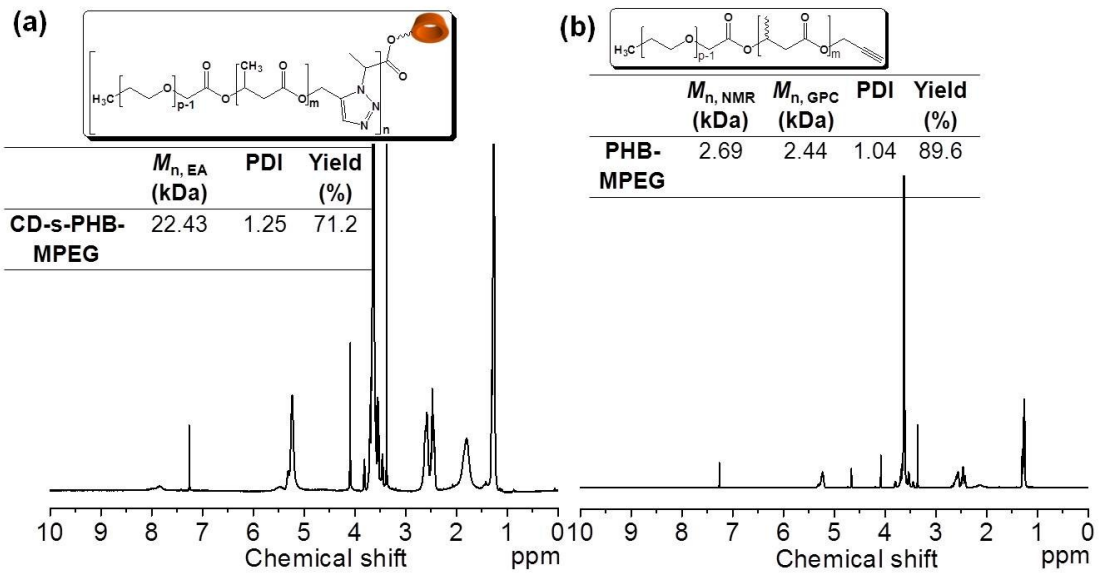


Figure S6. ^{1}H NMR spectrum of CD-s-PHB-MPEG (a) and its precursor PHB-MPEG (b) in $CDCl_3$.

4. Self-assembly properties of CD-s-PHB-Ada/DM-β-CD at various conditions

In order to observe the influence of preparation methods on the vesicle formation, we prepared DM-β-CD/CD-s-PHB-Ada(20:1) self-assemblies by three other methods as compared with the above used method. The three methods are (a) by simply injecting DMF solution of DM-β-CD/CD-s-PHB-Ada(20:1) into an aqueous solution, (b) by rehydrating CD-s-PHB-Ada film with DM-β-CD aqueous solution, (c) by adding water (pH=3) to DMF solution of DM-β-CD/CD-s-PHB-Ada-FITC(20:1) and dialyzing against water (pH=7) for doxorubicin hydrochloride (DOX) loading and DMF removal. Compared to the common method we used in this study, we changed the adding sequence of DMF and water in method (a). The influence of solvent was excluded in method (b). Method (c) was developed for drug delivery. DLS and TEM measurements showed that nanovesicles are formed by any of these methods, as shown in figure S7.

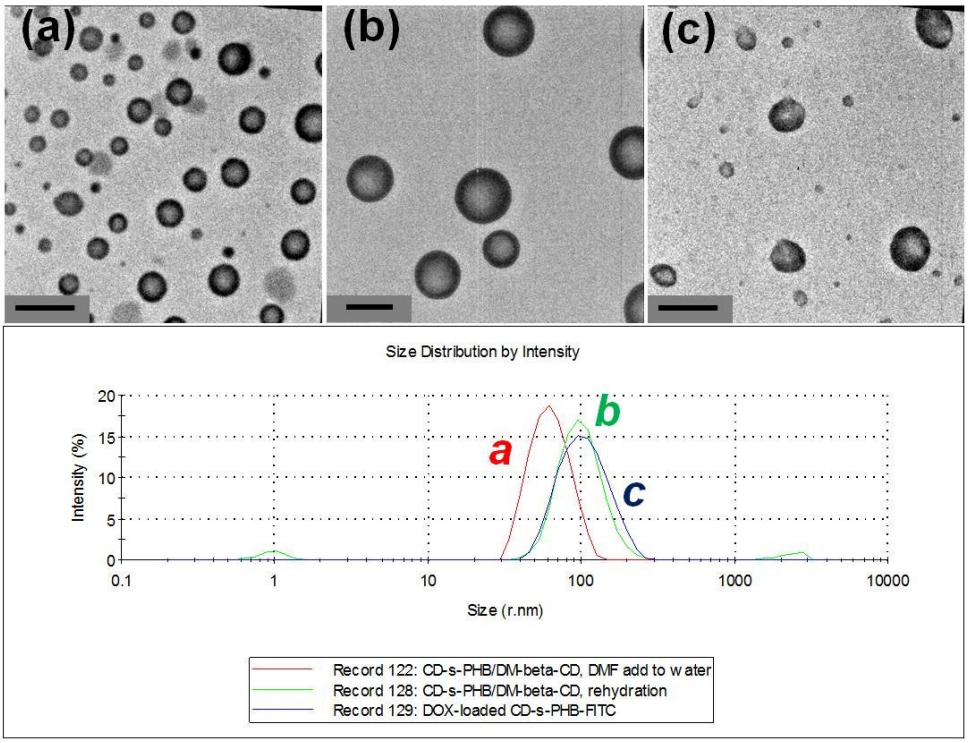


Figure S7. TEM images and particle size distribution of DM-β-CD/CD-s-PHB-Ada(20:1) aggregates prepared using different methods (a) by simply injecting DMF solution of DM-β-CD/CD-s-PHB-Ada(20:1) into an aqueous solution, (b) by rehydrating CD-s-PHB-Ada film with DM-β-CD aqueous solution, (c) by adding water (pH=3) to DMF solution of DM-β-CD/CD-s-PHB-Ada-FITC(20:1) and dialyzing against water (pH=7) for DOX loading and DMF removal. The scale bars represent 200 nm.

5. Self-assembly properties of control polymer (CD-s-PHB-MPEG)

In order to understand the self-assembly behavior of CD-s-PHB-Ada in the presence of DM-β-CD, the influence of DM-β-CD on the self-assembly behavior of the control polymer (CD-s-PHB-MPEG) was studied. All the samples were prepared at the same condition as that for CD-s-PHB-Ada.

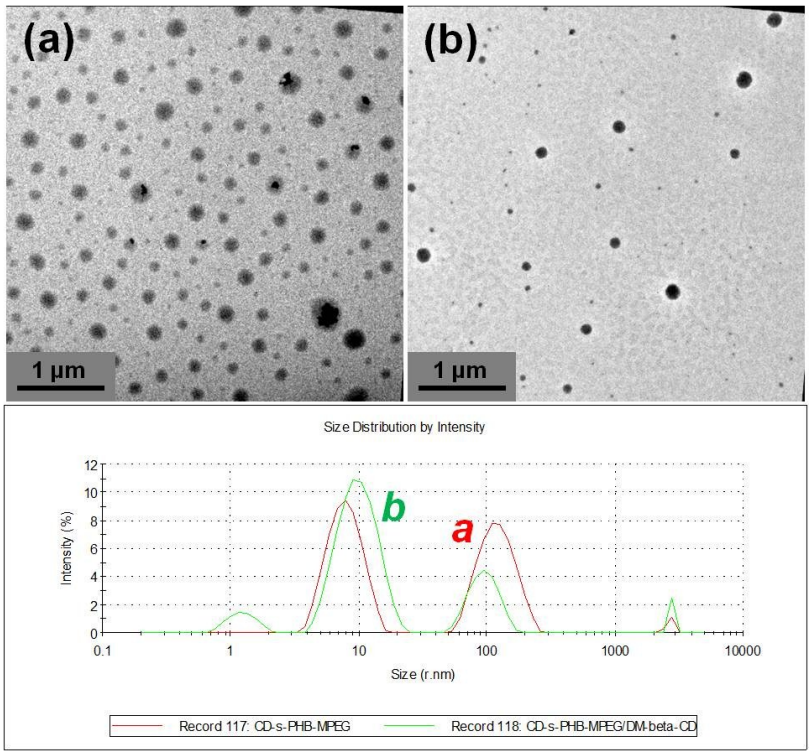


Figure S8. TEM images and particle size distribution of (a) CD-s-PHB-MPEG and DM-β-CD/CD-s-PHB-MPEG (20:1) aggregates.

The TEM images and particle size distribution of CD-s-PHB-MPEG and its complexes with DM-β-CD at weight ratio 20 were shown in Figure S8. From DLS and TEM results, it is seen that DM-β-CD has little influence on the self-assembly of CD-s-PHB-MPEG, which is easily understood since no complexation occurred in this system.

References

[1] a) Z. X. Zhang, X. Liu, F. J. Xu, X. J. Loh, E. T. Kang, K. G. Neoh, J. Li, *Macromolecules* **2008**, *41*, 5967-5970; b) J. Xu, S. Liu, *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, *47*, 404-419.

[2] K. L. Liu, S. H. Goh, J. Li, *Polymer* **2008**, *49*, 732-741.