Supplementary Information for:

UV light- and thermo-responsive supramolecular aggregates with tunable morphologies from the inclusion complexation of dendritic/linear polymers

Hui Zou\textsuperscript{a}, Weizhong Yuan\textsuperscript{*a}, Yeqiang Lu\textsuperscript{a} and Shanfeng Wang\textsuperscript{b}

\textsuperscript{a}School of Materials Science and Engineering, Tongji University, 201804, People’s Republic of China

\textsuperscript{b}Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Corresponding author

Weizhong Yuan

School of Materials Science and Engineering, Tongji University, 201804, People’s Republic of China

Tel: +86 21 69580234

E-mail address: yuanwz@tongji.edu.cn (W. Yuan)
1. Materials

β-cyclodextrin (β-CD, Aldrich) was dried 100 °C for 48 h under vacuum after recrystallization from water before use. ε-caprolactone (CL, Acros Organics, 99%) was purified with CaH₂ by vacuum distillation. Tin 2-ethylhexanoate (Sn(Oct)₂, Aldrich) was distilled under reduced pressure. The dendritic polyester (Perstorp Specialty Chemicals, Sweden; $M_n = 1747$ g·mol⁻¹; 16 terminal hydroxyl groups) was dried at 60 °C in vacuo for 24 h before use. 2-((N,N-Dimethylamino) ethyl methacrylate (DMAEMA, Acros Organics, 99%) was passed through a column of activated basic alumina to remove inhibitors. Copper bromide (CuBr, Alfa Aesar, 99%) was treated by stirring in glacial acetic acid and washed with ethanol several times. Methylene chloride (CH₂Cl₂, Sinopharm Chemical Reagent Co., Ltd.), tetrahydrofuran (THF, Sinopharm Chemical Reagent Co., Ltd.), N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.), and triethylamine (Et₃N, Aldrich) were dried over CaH₂ and distilled before use. 4-hydroxy-azo-benzene (Aldrich, 99%), 6-chlorohexanol (Aldrich, 99%), dicyclohexylcarbodiimide (DCC, Alfa Aesar, 99%), 4-dimethylaminopyridine (DMAP, Fluka, 98%), 2-bromoisobutyryl bromide (Aldrich, 99%), N,N′,N″,N‴,N′″-pentamethyldiethylenetriamine (PMDETA, Acros Organics, 99%), potassium carbonate (K₂CO₃, Sinopharm Chemical Reagent Co., Ltd., 99%), potassium iodide (KI, Sinopharm Chemical Reagent Co., Ltd., 99%), 4-methyl-benzenesulfonylchlorid (Alfa Aesar, 99%) and sodium azide (NaN₃, Alfa Aesar) were used as received. Propargyl 3-carboxylic-propanoate was prepared according to the literature.¹

2. Characterization

Attenuated total internal reflectance Fourier transform infrared (ATR FT-IR). ATR FT-IR spectra of samples were recorded on an EQUINOSS/HYPERION2000 spectrometer (Bruker, Germany). FT-IR spectra in Fig. S3 were measured at 25 °C.

Nuclear magnetic resonance (NMR). ¹H NMR spectra of samples were obtained from a Bruker AV 400 NMR spectrometer with CDCl₃, DMSO-d₆ or D₂O as the solvent. The chemical shifts were relative to tetramethylsilane. ¹H NMR spectra in Fig. S1, Fig. S2, Fig. S4, Fig. S6-S10 were measured at 25 °C.
**Gel permeation chromatography (GPC).** GPC analysis was carried out with a HLC-8320 (Tosoh, Japan) analysis system with two columns (TSK gel super AWM-H×2, R0091+R0093), using DMF with 10 mM LiBr as eluent at a flow rate of 0.6 mL·min⁻¹ at 40 °C. Monodisperse poly(methyl methacrylate) (PMMA) calibration kit was used as the calibration standard. GPC traces in Fig. S5 were measured at 25 ºC.

**Fluorescence spectroscopy (FS).** The fluorescence measurements were conducted on an F-2500 (Hitachi, Japan) fluorescence spectrophotometer with a xenon lamp source. The excitation wavelength for critical aggregation concentration (CAC) measurement and fluorescence spectra of Azo-PDMAEMA aqueous solutions was 335nm and 290 nm, respectively. Fluorescence measurements in this work were conducted at 25 ºC.

**UV-visible (UV-vis) absorption measurements.** UV-vis absorption studies were carried out using a U-3310 spectrophotometer (Hitachi, Japan) equipped with a temperature controller (0.1 ºC accuracy). UV-vis spectra in this work were conducted at 25 ºC. As for the transmittance measurements in Fig. 4a, the temperature of the sample cell was thermostatically controlled using an external super constant temperature bath. The solution was equilibrated for 10 min at each measuring temperature.

**Dynamic light scattering spectrophotometry (DLS).** The hydrodynamic radius ($R_h$) of the polymer aggregates was determined on a Malven Autosizer 4700 DLS spectrometer. The apparent $R_h$ was obtained by a cumulant analysis. The DLS plots in Fig. S13a’, Fig. S13b’, Fig. S14, Fig. S16, Fig. S17a’ and Fig. S19 were measured at 25 ºC.

**Transmission electron microscopy (TEM).** The morphology of polymer aggregates was observed with a JEOL JEM-2010 TEM at an accelerating voltage of 120 kV. The samples for TEM observation were prepared by placing 10 μL of polymer solutions on copper grids coated with thin films and carbon. The samples of Fig. 2a-c, Fig. 3a-c, Fig. S13a, Fig. S13b, Fig. S15, Fig. S17a, Fig. S18 and Fig. S20 were prepared at 25 ºC, while the samples of Fig. 4c-e and Fig. S24b were prepared at 50 ºC. All the samples were observed at 25 ºC by TEM.

**UV and Visible light irradiation.** A UV LED irradiator (UVATA, $\lambda_0 = 365$ nm) and
a Vis LED irradiator (CCS, $\lambda_0 = 500$ nm) were used to induce the photoisomerization of azobenzene moieties. The operations were conducted at 25 °C.

3 Experimental procedures

3.1 Synthesis of the dendrimer-like host polymer poly(ε-caprolactone) terminated with β-CD ((PCL-CD)$_{16}$)

Scheme S1 Synthesis route of the dendrimer-like host polymer (PCL-CD)$_{16}$.

**Synthesis of Mono-6-deoxy-6-azido-β-cyclodextrin (β-CD-N$_3$)**

β-CD-N$_3$ was synthesized by two steps according to the literature.$^2$ Firstly, mono-(6-O-(p-tolylsulfonyl))-β-cyclodextrin (β-CD-TsO) was synthesized by the reaction of β-CD with 4-methyl-benzenesulfonylchlorid. A typical procedure is given below. β-CD (50 g, 44.0 mmol) was dissolved in NaOH aqueous solution(500 mL, 0.4 mol/L) and then solution was cooled to 5 °C in an ice-bath. To the vigorously stirred solution was added p-toluensulfonyl chloride (35 g, 184 mmol) in small portions within 5 min. The mixture was stirred at 5 °C for 30 min and then was filtrated. The filtrate was neutralized with concentrated hydrochloric acid and stirred for 1 h. After filtering the reaction mixture and washing 3 times with deionized water, the white precipitate obtained was dried overnight at 60 °C (yield: 30%). Secondly, mono-6-deoxy-6-azido-β-cyclodextrin
(β-CD-N₃) was prepared the reaction between β-CD-TsO and sodium azide. β-CD-TsO (10 g, 7.76 mmol) was solved in 100 mL deionized water and heated to 80 °C. To this solution was added sodium azide (2.52 g, 38.8 mmol). The reaction was carried out at 80 °C for 6 h under stirring. Then the clear solution was poured in 600 mL acetone. The white powder of β-CD-N₃ was obtained by filtration and dried in vacuum at 60 °C until a constant weight was reached (yield: 90% ).

The products of mono-(6-O-(p-tolylsulfonyl))-β-cyclodextrin (β-CD-TsO) and mono-6-deoxy-6-azido-β-cyclodextrin (β-CD-N₃) were characterized by ¹H NMR (Fig. S1 and S2) and FT-IR (Fig. S3). All the protons signals assigned to β-CD-TsO and β-CD-N₃ can be clearly observed, indicating the successful preparation of the pure β-CD-TsO and β-CD-N₃. Moreover, a comparison of the FT-IR spectra of β-CD-TsO and β-CD-N₃ in Fig. S3 revealed the appearance of an absorbance peak at 2105 cm⁻¹ for β-CD-N₃, which is characteristic absorption peak of the azide group,²⁻⁴ further confirming the successful synthesis of β-CD-N₃.

The detailed assignments of the ¹H NMR spectra for β-CD-TsO and β-CD-N₃ are shown as follows:

β-CD-TsO: ¹H NMR (DMSO-d₆, δ, ppm): 2.43 (s, 3H, -SOO-C(CHCH₂CC₃)), 3.17-3.73 (m, 42H, C(2)H-C(6)H of β-CD), 4.49 (s, 6H, O(6)H of β-CD), 4.84 (m, 6H, C(1)H of β-CD), 5.74 (s, 14H, O(2)H, O(3)H of β-CD), 7.38-7.49 (d, 2H, -SOO-C(CHCH₂CC₃)), 7.69-7.80 (d, 2H, -SOO-C(CHCH₂CC₃)).

β-CD-N₃: ¹H NMR (DMSO-d₆, δ, ppm): 3.22-3.44 (m, C(2)H, C(4)H of β-CD overlapped with protons in H₂O), 3.50-3.80 (m, 38H, C(3)H, C(5)H, C(6)H of β-CD), 4.48 (s, 6H, O(6)H of β-CD), 4.78-4.90 (m, 6H, C(1)H of β-CD), 5.62-5.84 (m, 14H, O(2)H, O(3)H of β-CD).
**Fig. S1** $^1$H NMR of the $\beta$-CD-TsO.

**Fig. S2** $^1$H NMR of the $\beta$-CD-N$_3$. 
Fig. S3 FT-IR spectra of (a) β-CD-TsO, (b) β-CD-N₃ and (c) the host polymer (PCL-CD)₁₆.

**Synthesis of the dendrimer-star PCL (DPCL)**

The dendrimer-star PCL was synthesized by the ring opening polymerization of ε-caprolactone with the dendritic polyester as the initiator. CL (10 g, 87.7 mmol), dendritic polyester (0.958 g, 8.77 mmol of hydroxyl groups) and Sn(Oct)₂ (87.7μL) were added into a 25 mL round-bottom flask. The flask was degassed with three freeze-evacuate-thaw cycles. Then the flask was put into an oil bath at 120 °C under an argon atmosphere with magnetic stirring, and cooled to room temperature after polymerization for 24 h. The crude polymer was dissolved in methylene chloride and precipitated in methanol for three times. The purified dendrimer-star PCL was dried in a vacuum at room temperature until constant weight (yield: 96%).

¹H NMR spectrum of DPCL is shown in Fig. S4. All the protons signals of the polymer can be detected. The degree of polymerization of CL on each arm was obtained from the integration of the proton signals at 4.04 ppm (peak d) and 3.63 ppm (peak d’). The number-average molecular weight ($M_{n,NMR}$) of DPCL can be calculated according to equation (1).

$$M_{n,NMR} = \left(\frac{I_d}{I_{d'}} + 1\right) \times 114 \times 16 + 1747$$  \hspace{1cm} (1)
Here, 114 is the molecular weight of CL monomer, 16 is the number of the PCL arms in DPCL, and 1747 is the molecular weight of the initiator of the dendritic polyester. 

\[ \left( \frac{I_d}{I_d'} + 1 \right) \] 

The \( M_{n,NMR} \) was 19980 g·mol\(^{-1}\). It should be noticed that \( I_d' \) refers to the degree of the polymerization (DP) of CL on each arm, and the result is \( \sim 10 \).

The GPC trace of DPCL is shown in Fig S5. The trace is monomodal with a number-average molecular weight of 15426 g·mol\(^{-1}\). It can be seen that the value of \( M_n \) measured by GPC was lower than that calculated by \(^1\)H NMR spectra. This is because the hydrodynamic volumes of star-shaped polymers are smaller than those of linear polymers used for calibration. Therefore, we selected \( M_{n,NMR} \) as accurate molecular weight for following calculation.

The detailed assignments of the \(^1\)H NMR spectrum for DPCL are shown as follows:

\(^1\)H NMR (CDCl\(_3\), \( \delta \), ppm): 0.78-1.29 (-CH\(_3\) in dendrimer), 1.38 (m, -OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 1.63 (-OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 2.29 (-OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 3.63 (-OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)OH), 4.04 (-OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 4.12-4.37 (-CH\(_2\)- in dendrimer).
**Synthesis of the alkynyl-modified DPCL**

The alkynyl-modified DPCL was synthesized through the esterification reaction of DPCL with excess propargyl 3-carboxylic-propanoate. The general procedure is as follows. The DPCL (2.50 g, 2.0 mmol of hydroxyl groups), propargyl 3-carboxylic-propanoate (1.56 g, 10.0 mmol), DMAP (0.244 g, 2.0 mmol), and DCC (0.823 g, 4.0 mmol) were dissolved in 50 mL of anhydrous CH$_2$Cl$_2$. The reaction was carried out at room temperature for 48 h under vigorous stirring. The reaction byproduct dicyclohexylcarbodiurea (DCU) was removed by filtration. The filtered solution was concentrated by a rotary evaporator and then precipitated in cold methanol for three times. The purified alkynyl-modified DPCL was obtained by filtration and dried in vacuum at room temperature until a constant weight is reached (yield: 91%).

$^1$H NMR spectrum of alkynyl-modified DPCL is shown in Fig. S6. Comparing with the $^1$H NMR spectrum of DPCL in Fig. S4, new peaks at 2.45 ppm (peak g), 2.66 ppm (peak e) and 4.69 ppm (peak f) can be detected in Fig. S6, revealing that the terminal hydroxyl groups of DPCL had reacted with propargyl 3-carboxylic-propanoate. Meanwhile, the peak at 3.66 ppm (peak d’, Fig. S4) disappeared completely, suggesting the complete conversion of DPCL to alkynyl-modified DPCL. The $M_{n,NMR}$ of alkynyl-
modified DPCL can be calculated according to equation (2).

\[
M_{n,NMR} = \frac{I_d}{I_f} \times 114 \times 16 + 3955 \tag{2}
\]

Here, 114 is the molecular weight of CL monomer as above, 16 is the number of the PCL arms in alkynyl-modified DPCL, and 3955 is the molecular weight of the groups out of the repeating CL units. The \(M_{n,NMR}\) of alkynyl-modified DPCL was calculated as 22190 g·mol\(^{-1}\). The detailed assignments of the \(^1\)H NMR spectrum for alkynyl-modified DPCL are shown as follows:

\(^1\)H NMR (CDCl\(_3\), \(\delta\), ppm): 1.19-1.30 (-CH\(_3\) in dendrimer), 1.38 (m, -OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 1.64 (m, -OOCCH\(_2\)CH\(_2\)CH\(_2\)H\(_2\)CH\(_2\)O-), 2.30 (m, -OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 2.45 (s, -COOCH\(_2\)C≡CH), 2.66 (s, -OOCCH\(_2\)CH\(_2\)CH\(_2\)COO-), 4.05 (m, -OOCCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-), 4.12-4.34 (-CH\(_2\)- in dendrimer), 4.69 (s, -COOCH\(_2\)C≡CH).

**Fig. S6** \(^1\)H NMR of alkynyl-modified DPCL.

**Synthesis of the host polymer (PCL-CD)\(_{16}\)**

The host polymer (PCL-CD)\(_{16}\) was synthesized by the click reaction of between alkynyl-modified DPCL and an excess of \(\beta\)-CD-N\(_3\). A dried 50 mL round-bottom flask with a magnetic stirrer was charged with alkynyl-modified DPCL (1.20 g, 0.86 mmol of alkynyl groups), \(\beta\)-CD-N\(_3\) (3.98 g, 3.44 mmol), CuBr (0.123 g, 0.86 mmol),
PMDETA (182 μL, 0.86 mmol), and anhydrous DMF (30 mL). The flask was degassed with three freeze-evacuate-thaw cycles and back filled with argon. Then, the reaction was performed at 50 °C for 24 h. After being cooled to room temperature, the reaction flask was exposed to air, and the crude product was purified by dialysis (molecular weight cut-off: 8000-14000 Da) against water to remove the catalyst and unreacted β-CD-N₃. The final product was collected by freeze-drying.

¹H NMR spectrum of the host polymer (PCL-CD)₁₆ is shown in Fig. S7. The peaks attributed to β-CD groups can be detected clearly. Moreover, a new peak at 8.10 ppm, which is attributed to the methane proton of the 1,2,3-triazole group. Meanwhile, the methylene protons next to the alkynyl groups changed from 4.69 ppm (peak f in Fig. S6) to 5.08 ppm (peak f in Fig. S7), and the characteristic absorption peak of the azide group (2105 cm⁻¹) disappeared after click reaction in the FT-IR spectrum as shown in Fig. S3. All these indicate that the click chemistry between alkynyl-modified DPCL and β-CD-N₃ had happened. The conversion ratio (C%) of alkynyl-modified DPCL to the host polymer (PCL-CD)₁₆ can be calculated according to equation (3).

\[
C\% = \frac{I_g}{I_a} \times 10 \times 2 \times 100%
\]  

(3)

Here, 10 is the DP of CL on every arm calculated from the ¹H NMR (Fig. S4), and 2 is the proton number ratio of methylene (peak a) to methane (peak g). The C% of alkynyl-modified DPCL to (PCL-CD)₁₆ is ~97%. This high conversion ratio resulted from the high efficiency of the click chemistry, as well as the excess feeding of β-CD-N₃. So we can see that the host polymer (PCL-CD)₁₆ had been successfully obtained.

The \(M_{n,\text{NMR}}\) of (PCL-CD)₁₆ can be calculated according to equation (4).

\[
M_{n,\text{NMR}} = 22190 + 1160 \times 16
\]  

(4)

Here, 22190 is the number-average molecular weight of alkynyl-modified DPCL calculated by ¹H NMR, 1160 is the number-average molecular weight of β-CD-N₃, and 16 is the number of the PCL arms in the host polymer (PCL-CD)₁₆. The \(M_{n,\text{NMR}}\) of (PCL-CD)₁₆ was calculated as 40750 g·mol⁻¹. The GPC trace of (PCL-CD)₁₆ is shown in Fig. S5, and the value of \(M_n\) measured by GPC was 35467 g·mol⁻¹.

The detailed assignments of the ¹H NMR spectrum for the host polymer (PCL-CD)₁₆
are shown as follows:

\(^1\text{H NMR (DMSO-}d_6, \delta, \text{ ppm): 0.49-1.05 (-C}_3\text{H}_3\text{ in dendrimer), 1.28 (m, -OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O-), 1.52 (m, -OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O-), 2.26 (m, -OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O-), 2.38-2.63 (-OOCCH}_2\text{CH}_2\text{COO-}, overlapped with the solvent residual peak of DMSO-}d_6\text{), 3. 50-6.24 (m, m, O(6)H and -C}_3\text{H}_3\text{ of }\beta\text{-CD, overlapped with methylene proton in the repeating unit in PCL), 4.01 (m, -OOCCH}_2\text{CH}_2\text{CH}_2\text{H}_2\text{O-), 5.08 (s, -COOCCH}_2\text{ next to the 1, 2, 3-triazole group) 8.10 (s, -C}_3\text{H}_3\text{ of the 1, 2, 3-triazole group).}

Fig. S7 \(^1\text{H NMR of the host polymer (PCL-CD)}_{16}\).

3.2 Synthesis of the guest polymer Azo-PDMAEMA

![Synthesis of Azo-C\(_6\)-OH](image)

**Scheme S2** Synthesis route of the guest polymer Azo-PDMAEMA.

*Synthesis of Azo-C\(_6\)-OH*
The Azo-C$_6$-OH was synthesized by Williamson etherification of 4-hydroxy-azo-benzene with 6-chlorohexanol. The procedure is as follows. 4-hydroxy-azo-benzene (9.90 g, 50.00 mmol), 6-chloro-1-hexanol (10.20 g, 75.00 mmol), potassium carbonate (10.35 g, 75.00 mmol) and a trace amount of potassium iodide were added into DMF (200 mL). The reaction was carried out at 90 °C under stirring for 12 h. The reaction mixture was poured into a large amount of deionized water, and then extracted with chloroform. The organic phase was collected and MgSO$_4$ was added into the chloroform solution. The crude product was obtained by removing the solvent through rotary evaporator. The final product was obtained after being purified by recrystallization and dried in vacuum at room temperature until constant weight.

$^1$H NMR spectrum of Azo-C$_6$-OH is shown in Fig. S8. Well-resolved proton signals assigned to Azo-C$_6$-OH can be clearly observed. Meanwhile, the integral area ratio of peak e (4.05 ppm) to peak c (7.96 ppm) is 1:2, indicating the obtaining of the pure product. The detailed assignments of the $^1$H NMR spectrum are shown as follows:

$^1$H NMR (CDCl$_3$, $\delta$, ppm): 1.38-1.58 (m, 4H, -CH$_2$-CH$_2$-CH$_2$-CH$_2$-OH), 1.63 (m, 2H, -CH$_2$-CH$_2$-OH), 1.85 (m, 2H, -Ph-O-CH$_2$-CH$_2$-), 3.68 (t, 2H, -CH$_2$-OH), 4.05 (t, 2H, -CH$_2$-OH), 6.97-7.96 (m, 9H, -CH- of the azobenzene group).

![Fig. S8 $^1$H NMR of Azo-C$_6$-OH.](image)

**Synthesis of Azo-C$_6$-Br**
The Azo-C₆-Br was synthesized through the reaction between Azo-C₆-OH and an excess of 2-bromoisobutyryl bromide. Azo-C₆-OH (4.80 g, 16.10 mmol) and Et₃N (1.63 g, 16.14 mmol) were dissolved in anhydrous CH₂Cl₂ (60 mL) under an argon atmosphere. The mixture was stirred and cooled to 0 °C in an ice bath. 2-bromoisobutyryl bromide (18.49 g, 80.44 mmol) in anhydrous CH₂Cl₂ (36 mL) was added dropwise to the mixture within 1 h at 0 °C. The reaction was carried out at 0 °C for 2 h and then stirred for 48 h at room temperature. The reaction mixture was concentrated by a rotary evaporator and then precipitated in cold ethanol. The product was obtained after filtration and dried at room temperature in vacuum until constant weight.

¹H NMR of Azo-C₆-Br is shown in Fig. S9. Comparing with the ¹H NMR spectrum of Azo-C₆-OH (Fig. S8), a new peak at 1.93 ppm, which corresponds to the methyl protons in the bromoethyl group (-C(CH₃)₂Br), can be observed in Fig. S9. This means that the terminal hydroxyl groups of Azo-C₆-OH have reacted with 2-bromoisobutyryl bromide. In the meantime, the peak at 3.68 ppm (peak i, Fig. S8) disappeared completely and a new peak at 4.20 ppm (peak i, Fig. S9) appeared, revealing the complete conversion of Azo-C₆-OH to Azo-C₆-Br. The detailed assignments of the ¹H NMR spectrum are shown as follows:

¹H NMR (CDCl₃, δ, ppm): 1.51 (m, 4H, -CH₂CH₂CH₂CH₂COO-), 1.74 (m, 2H, -CH₂CH₂CH₂CH₂COO-), 1.84 (m, 2H, -Ph-O-CH₂CH₂CH₂CH₂CH₂COO-), 1.93 (s, 6H, -COOC(H₃)₂Br), 4.04 (t, 2H, -Ph-O-CH₂CH₂CH₂CH₂COO-), 4.20 (t, 2H, -CH₂CH₂CH₂CH₂CH₂COO-), 6.96-8.00 (m, 9H, -CH- of the azobenzene group).
Synthesis of the guest polymer Azo-PDMAEMA

The guest polymer Azo-PDMAEMA was synthesized by atom transfer radical polymerization (ATRP) of DMAEMA monomer using Azo-C₆-Br as the initiator. A typical procedure is as below. A dried reaction flask with a magnetic stirrer was charged with Azo-C₆-Br (0.90 g, 2.01 mmol), DMAEMA (12.62 g, 80.38 mmol), CuBr (0.29 g, 2.01 mmol), PMDETA (425 μL, 2.01 mmol), and anhydrous THF (25 mL). The flask was degassed with three freeze-evacuate-thaw cycles. Then, the polymerization was performed at 60 °C under an argon atmosphere with magnetic stirring. After 6 h, the reaction system was exposed to air to stop the polymerization. The mixture was diluted with THF and passed through a neutral alumina column to remove the copper catalysts. The eluent was concentrated by using a rotary evaporator and then precipitated in the cold n-hexane for three times. The product was dried in a vacuum at 35 °C until a constant weight was obtained (yield: 95%).

¹H NMR of the guest polymer Azo-PDMAEMA is shown in Fig. S10. The proton signals attributed to the PDMAEMA segments can be detected clearly. The DP of DMAEMA was calculated from the integration of the proton signals at 4.06 ppm (peak g) and 6.95 ppm (peak d). The $M_{n,NMR}$ of Azo-PDMAEMA can be calculated according to equation (5).

$$M_{n,NMR} = \frac{I_g}{I_d} \times 157 + 447$$  (5)
Here, 157 is the molecular weight of DMAEMA monomer and 447 is the molecular weight of the initiator Azo-C₆-Br. The $M_{n,\text{NMR}}$ was 6260 g·mol⁻¹. The GPC trace of Azo-PDMAEMA is shown in Fig. S5 and the $M_n$ value measured by GPC was 6525 g·mol⁻¹.

The detailed assignments of the $^1$H NMR spectrum for the guest polymer Azo-PDMAEMA are shown as follows:

$^1$H NMR (CDCl₃, $\delta$, ppm,): 0.76-1.18 (m, -CH$_2$C(CH$_3$)(Br)-), 1.72-2.08 (m, -CH$_2$C(CH$_3$)(Br)-), 2.28 (s, -N(CH$_3$)$_2$), 2.56 (s, -COOCH$_2$CH$_2$N(CH$_3$)$_2$), 4.06 (s, -COOCH$_2$CH$_2$N(CH$_3$)$_2$), 6.95-7.98 (m, -CH- of the azobenzene group).

Fig. S10 $^1$H NMR of the guest polymer Azo-PDMAEMA.

3.3 Self-assembly in aqueous solutions

**Self-assembly of the host polymer (PCL-CD)$_{16}$ and guest polymer Azo-PDMAEMA**

A typical procedure for the self-assembly of the host polymer (PCL-CD)$_{16}$ was as follows: (PCL-CD)$_{16}$ (20 mg) was dissolved in DMF (8 mL) and then deionized water (10 mL) was added into the solution at a rate of 1 mL·h⁻¹ under vigorous stirring. The mixed solution was stirred for another 6 h and then dialyzed against deionized water to remove DMF for 4 days. The obtained solution was diluted to 0.5 mg·mL⁻¹ with deionized water and equilibrated at 25 °C for 48 h.

The procedure for the self-assembly of Azo-PDMAEMA was the same as that of (PCL-CD)$_{16}$. 
Self-assembly of the supramolecules

The supramolecular aggregates with different (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio were prepared as follows: 20 mg of the (PCL-CD)$_{16}$/Azo-PDMAEMA mixtures were dissolved in DMF (8 mL). The (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio in the (PCL-CD)$_{16}$/Azo-PDMAEMA mixtures were 1:1, 1:8 and 1:16, in which the molar ratio of β-CD groups to Azo groups was 16:1, 16:8, and 16:16, respectively. The solutions were stirred for 24 hours at room temperature. Then 10 mL of deionized water was added slowly into the solutions at a rate of 0.25 mL·h$^{-1}$ under vigorous stirring. Subsequently, the solutions were stirred for another 6 h and then dialyzed against deionized water to remove DMF for 4 days. The obtained solutions were diluted to 0.5 mg·mL$^{-1}$ with deionized water and equilibrated at 25 °C for 48 h.

4. Estimation of the association constant ($K_a$) between (PCL-CD)$_{16}$ and Azo-PDMAEMA

The association constant ($K_a$) between the host polymer (PCL-CD)$_{16}$ and the guest polymer Azo-PDMAEMA in aqueous solution was investigated by $^1$H NMR measurement,\textsuperscript{5-7} in which the concentration of Azo-PDMAEMA was kept at 0.05 mM. Fig. S11a shows the $^1$H NMR spectra of Azo-PDMAEMA in the presence of varying concentrations (PCL-CD)$_{16}$. It can be observed that the signals due to the protons of Azo groups shifted downfield when the concentration of (PCL-CD)$_{16}$ increased, suggesting the interaction between (PCL-CD)$_{16}$ and Azo-PDMAEMA. The reciprocals of the peak shifts (1/Δδ) were then used to calculate $K_a$ according to Hidebrand-Benesi equation.

\[
\frac{1}{\Delta \delta} = \frac{1}{K_a[C(D)] \Delta \delta_{max}} + \frac{1}{\Delta \delta_{max}} \quad (6)
\]

Here, $\Delta \delta$ is the difference of the chemical shift observed for Azo-PDMAEMA in the absence and presence of (PCL-CD)$_{16}$, $\Delta \delta_{max}$ is the difference in chemical shift between that observed in Azo-PDMAEMA and that observed in the complex,\textsuperscript{6} and [CD] is the concentration of β-CD groups in (PCL-CD)$_{16}$. The value of $K_a$ was obtained from the intercept and the slope of the Benesi-Hildebrand plot as shown in Fig. S11b. The $K_a$
between (PCL-CD)\textsubscript{16} and Azo-PDMAEMA is 780 M\textsuperscript{-1} in aqueous solution, which is about a half smaller than simple molecular complex such as β-CD/Azo (1700 M\textsuperscript{-1}).

**Fig. S11** (a) \textsuperscript{1}H NMR spectral of Azo-PDMAEMA (0.05 mM) in the presence of (PCL-CD)\textsubscript{16} in D\textsubscript{2}O, the molar concentrations of β-CD groups in (PCL-CD)\textsubscript{16} were 0, 0.003125, 0.00625, 0.0125, 0.025, 0.05, and 0.10 mM from A to G, and (b) Benesi-Hildebrand plot of 1/Δδ against 1/[CD].

**5. Critical aggregation concentration (CAC) measurements**

_The CACs of the host polymer (PCL-CD)\textsubscript{16} and guest polymer Azo-PDMAEMA_

The CACs of the host polymer (PCL-CD)\textsubscript{16} and guest polymer Azo-PDMAEMA in aqueous solutions were measured using pyrene as the fluorescent probe.

The CAC measurement for (PCL-CD)\textsubscript{16} was conducted as follows. 12.0 mg of pyrene was dissolved in 20 mL of acetone and then 10 μL of the solution was added into each cuvette. The acetone was allowed to evaporate. Then 2.0 mL of (PCL-CD)\textsubscript{16} aqueous solutions ranging from 0.488 mg·L\textsuperscript{-1} to 500 mg·L\textsuperscript{-1} were added into the pyrene-containing cuvette separately. Upon sonication for 10 min, the solutions were kept at room temperature and equilibrated for 24 h before fluorescent emission measurements with an excitation wavelength of 335 nm. The spectra were recorded in the 340-600 nm wavelength range. For each spectrum obtained, the intensity ratio of the first and third peaks, \(I_1/I_3\) was calculated. The CAC was estimated as the concentration at which \(I_1/I_3\)
began to drop, suggesting that the aggregation of the polymer occurred. The result showed that the CAC of (PCL-CD)$_{16}$ was about 4.82 mg·L$^{-1}$ (Fig. S12a).

The CAC measurement procedure for the guest polymer Azo-PDMAEMA was the same as above, and the CAC of Azo-PDMAEMA was 106.2 mg·L$^{-1}$ (Fig. S12b).

Fig. S12 CAC of (a) the host polymer (PCL-CD)$_{16}$ and (b) the guest polymer Azo-PDMAEMA in aqueous solutions.

Fig. S13 TEM images (a, b) and DLS data (a’, b’) of the (a, a’) host polymer (PCL-CD)$_{16}$ aggregates and (b, b’) guest polymer Azo-PDMAEMA aggregates (Concentration: 0.5 mg·mL$^{-1}$).
The CACs of the supramolecules

The CACs of the supramolecules (PCL-CD)\textsubscript{16}/Azo-PDMAEMA with the molar ratio of (PCL-CD)\textsubscript{16}:Azo-PDMAEMA being 1:1, 1:8, and 1:16 in aqueous solutions were also measured using pyrene as the fluorescent probe. The CAC measurement procedure for the supramolecules with (PCL-CD)\textsubscript{16}:Azo-PDMAEMA ratio being 1:1, 1:8 and 1:16 was the same as that for (PCL-CD)\textsubscript{16}. And the CAC values of the supramolecules with (PCL-CD)\textsubscript{16}:Azo-PDMAEMA ratio being 1:1, 1:8 and 1:16 were 6.08 mg·L\textsuperscript{-1} (Fig. S14a), 24.43 mg·L\textsuperscript{-1} (Fig. S14b), and 51.90 mg·L\textsuperscript{-1} (Fig. S14c), respectively.

Fig. S14 CAC of the supramolecules with the molar ratio of (PCL-CD)\textsubscript{16}:Azo-PDMAEMA being (a) 1:1, (b) 1:8, and (c) 1:16.

5. Other Supplementary Results
**Fig. S15** TEM images of the supramolecular aggregates at the molar ratio of (PCL-CD)$_{16}$:Azo-PDMAEMA being (a) 1:1, (b) 1:8, and (c) 1:16 (Concentration: 0.5 mg·mL$^{-1}$).

**Fig. S16** DLS data of the supramolecular aggregates with (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio of (a) 1:1, (b) 1:8, and (c) 1:16 (Concentration: 0.5 mg·L$^{-1}$).
Fig. S17 TEM images (a) and DLS data (a’) of the guest polymer Azo-PDMAEMA aggregates after UV irradiation for 30 s (Concentration: 0.5 mg·L⁻¹).

Fig. S18 TEM images of the supramolecular aggregates with the molar ratios of (PCL-CD)₁₆:Azo-PDMAEMA being (a) 1:1, (b) 1:8, and (c) 1:16 after UV-light irradiation for 30 s (Concentration: 0.5 mg·L⁻¹).

Fig. S19 DLS data of the supramolecular aggregates with (PCL-CD)₁₆:Azo-PDMAEMA molar ratio of (a) 1:1, (b) 1:8, and (c) 1:16 after UV irradiation for 30 s (Concentration: 0.5 mg·L⁻¹).
**Fig. S20** TEM images of supramolecular aggregates with the molar ratio of \((\text{PCL-CD})_{16}:\text{Azo-PDMAEMA}\) being (a) 1:1, (b) 1:8 , and (c) 1:16 after UV light irradiation at 365 nm for 30 s and subsequent visible light irradiation at 500 nm for 60 s (Concentration: 0.5 mg·L\(^{-1}\)).

**Fig. S21** Periodical change of UV-vis spectroscopy under the control of light for the supramolecule aqueous solutions with \((\text{PCL-CD})_{16}:\text{Azo-PDMAEMA}\) molar ratio of 1:16 (Concentration: 0.5 mg·mL\(^{-1}\)).
Fig. S22 UV-vis spectra of the supramolecule aqueous solutions with (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio of 1:1 upon (a) irradiation at 365 nm for different times, (b) subsequent irradiation at 500 nm for different times, and (c) periodical change of UV-vis spectroscopy under the control of light for the supramolecule aqueous solutions with (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio of 1:1 (Concentration: 0.5 mg·mL$^{-1}$).

Fig. S23 UV-vis spectra of the supramolecule aqueous solutions with (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio of 1:1 (Concentration: 0.5 mg·mL$^{-1}$).
PDMAEMA molar ratio of 1:8 upon (a) irradiation at 365 nm for different times, (b) subsequent irradiation at 500 nm for different times, and (c) periodical change of UV-vis spectroscopy under the control of light for the supramolecule aqueous solutions with (PCL-CD)$_{16}$:Azo-PDMAEMA molar ratio of 1:8 (Concentration: 0.5 mg·mL$^{-1}$).

![Figure S24](image)

**Fig. S24** (a) Temperature dependence of hydrodynamic radius ($R_h$) of the guest polymer Azo-PDMAEMA aqueous solution and (b) TEM images of the Azo-PDMAEMA aggregates at 50 °C (Concentration: 0.5 mg·L$^{-1}$).

**Reference:**


