Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Self-Assembly of Alkyl-Perylenebisdiimide–DNA Amphiphiles and Control of Its Morphology through Cyclodextrin-based Host–Guest Interaction

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1. Materials and Methods

All the materials were obtained from commercial suppliers and were used without further purification, unless otherwise stated. Perylene-3,4,9,10-tetracarboxylic dianhydride, isooctyl amine, (S)-3-amino-1,2-propanediol, 5-ethylthioltetrazole, 4,4-dimethoxy triphenylmethyl chloride and 2-cyanoethyl-N,N-diisopropyl chlorophosphoride were purchased from energy-chemical. All of the DNA sequences were obtained from IDOBIO Company (Beijing, China). The water used in all of the experiments was Milli Q deionized water (18.2 MΩ.cm).

DNA sequences:

CPG-D18: 5'-OH-TACTACACCACCACAACA-3'

Complementary DNA: 5'- HS-TGTTGTGGTGGTGTA-3'

Non-complementary DNA: 5'-HS-TTCATCTTTCACCTA-3'

Matrix-assisted laser desorption-ionization (time of flight) mass spectrometry (MALDI-TOF): MALDI-TOF was performed on a Bruker Biflex III MALDI-TOF spectrometer. Samples were dissolved in 50 μL Milli-Q water at a concentration of 30 μM.

TEM measurements: The sample was applied to a carbon grid by adding a 7 μL drop of sample solution to the grid and carefully removed by using a filter paper after 2 min immersion. The grid was allowed to dry for at least 15 min before applying 7 μL of a 1 wt% uranyl acetate aqueous solution, which was removed after 20 s. The grid was allowed to dry for at least 15 min again. Samples were studied on a JEOL JEM-2100 TEM (Jeol, Japan).

Dynamic light scattering (DLS) experiments: The experiments were performed on Nicomp 380 Z3000. The volume of the samples were 100 μL. The number of cycles of each sample was 3 times, and the time of each cycle was 3 minutes.

Fluorescence measurements: The fluorescence spectra were recorded at room temperature in a quartz cuvette on a PerkinElmer SL-55 Fluorescence Spectrometer. The excitation wavelength was 505 nm, and the emission wavelengths were in the range from 530 to 750 nm with excitation slits of 5 nm and emission slits of 20 nm.

UV/Vis measurements: The experiments were performed on a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K.

^{1}H NMR measurements: All ^{1}H NMR spectra were collected on Agilent 600 MHz $CDCl_3$.

General procedure for preparation of DNA modified AuNPs[1]:

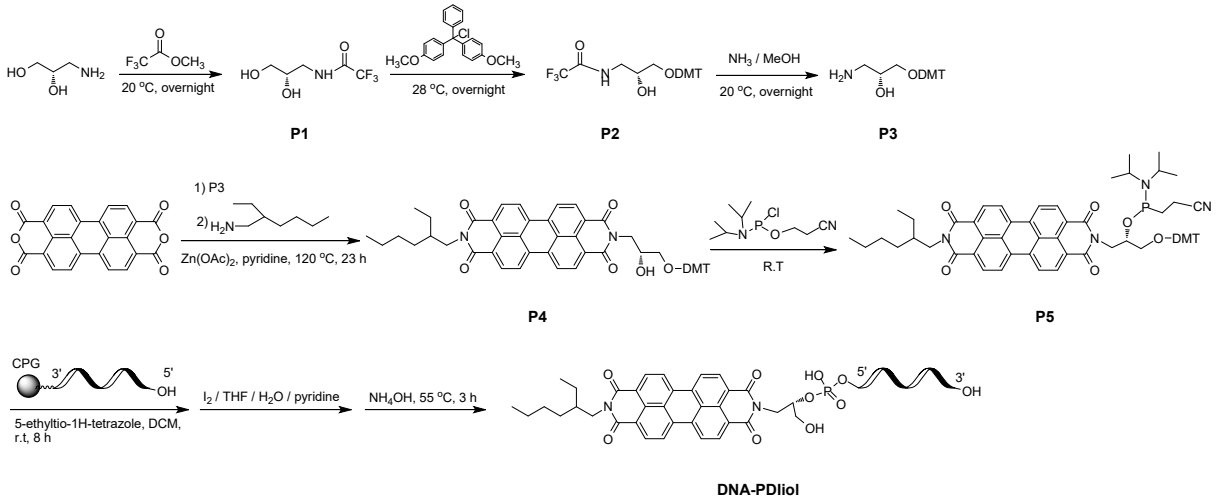
A solution of DNA (10 μM, 45.48 μL) was added into the 5 nm AuNPs (22.74 nM, 100 μL) solution. 3 μL 5 × TBE buffer and 1.52 μL H_2O were added. And then, adding different volumes of NaCl solution (2 M) in turn, the concentration of sodium chloride in the solution gradually increased from 50 mM to 300 mM. The mixed solution was incubated at room temperature overnight and then centrifugation at 15 000 r/s for 15 min to remove the free DNA. After removing the supernatant, the dark-red precipitate was washed three times with pH 8.0, 0.1 × TBE buffer containing 100 mM NaCl by successive centrifugation and finally re-dispersed in 7 μL fresh pH 8.0, 10 mM NaCl, 0.1 × TBE buffer.

Hybridization process:

109.1 nM (7 μL) complementary DNA modified AuNPs were incubated with D18-PDIiol micelles solution (2 μL) and D18-PDIiol@β-CD nanofibers solution (2 μL) in 0.1 × TBE (pH 8.0) buffer at room temperature overnight, respectively. As a control, non-complementary DNA modified AuNPs experiments were conducted with same treatment as the complementary DNA.

2. Synthesis and Characterization of D18–PDIiol Amphiphiles

2.1 Synthesis of D18–PDIiol Amphiphiles



Scheme S1. Synthetic route of D18–PDIiol conjugates

Compounds P**3** was synthesized according to the related literatures.[2a] 1H NMR (600 MHz, $CDCl_3$, 298K): δ 7.40-7.36 (m, 2H), 7.25 (dd, J = 22.7, 81 Hz, 6H), 7.16 (t, J = 7.3 Hz,1H), 6.78 (d, J = 8.6 Hz, 4H), 3.82 (dp, J = 9.1, 5.3, 4.8 Hz,1H), 3.73 (s, 6H), 3.43 (s, 2H), 3.10 (d, J = 5.2 Hz, 2H), 2.91-2.71 (m, 2H).

Compounds P**4** were synthesized according to the related literatures.[2b] 1H NMR (600 MHz, $CDCl_3$, 298K): δ 8.64 (d, J = 7.9 Hz, 4H),8.55 (dd, J = 8.1, 4.2 Hz, 4H), 7.48 (d, J = 7.8 Hz, 2H), 7.35 (dd, J = 8.9, 2.7 Hz, 4H), 7.27 (t, J = 7.6 Hz, 2H), 6.81 (dd, J = 9.0, 2.9 Hz, 4H), 4.64 (dd, J = 13.8, 9.3 Hz, 1H), 4.31 (dd, J = 13.9, 3.4 Hz, 1H), 4.23 (s, 1H), 4.19 – 4.09 (m, 3H), 3.76 (d, J = 2.3 Hz, 6H), 3.18 (q, J = 6.0 Hz, 2H), 1.97 (s, 2H), 1.31 (q, J = 6.7, 6.0 Hz, 8H), 0.88 (dd, J = 8.7, 5.9 Hz, 9H).

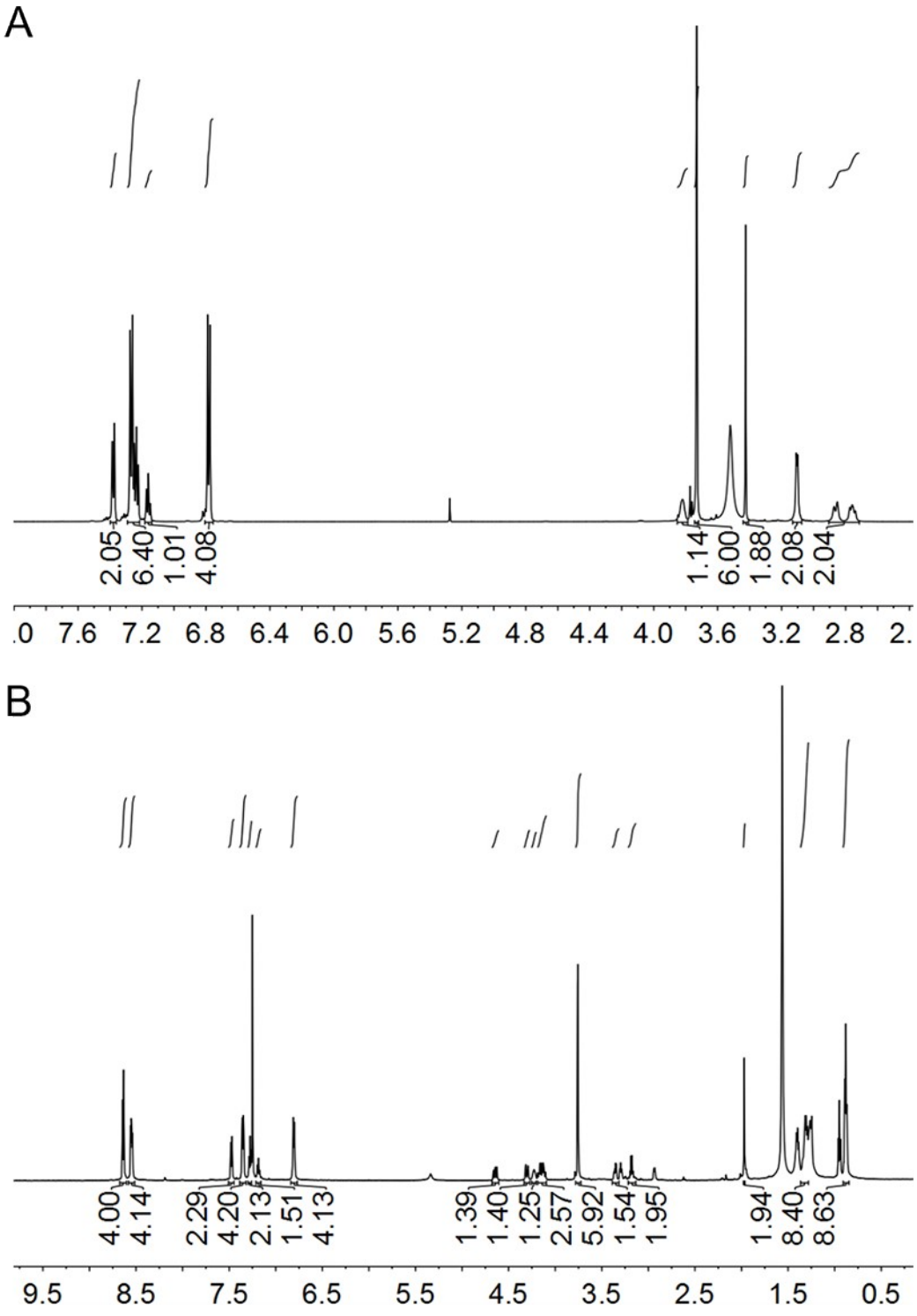


Figure S1. 1HNMR (600 MHz, $CDCl_3$, 298K) of compound P3(A) and P4(B).

Compounds D18–PDIiol were synthesized according to the related literature.[3]

Weighed 0.176 g of **P4** in a 24-necked round-bottom flask, vacuum and charge with argon. N,N-diisopropylethylamine (0.170 mL, 1 mmol) and 2-cyanoethyl diisopropyl chlorophosphoramidite (0.140 mL, 0.6 mmol) were added under argon atmosphere and stirred for one hour at room

temperature. After the reaction was finished, saturated $NaHCO_3$ was added for quenching, which was extracted with saturated $NaHCO_3$, distilled water and saturated NaCl solution, respectively, and then spin-dried in argon atmosphere to obtain product **P5**.

CPG-attached oligodeoxynucleotide chain (0.002 mmol) and ethylthiotetrazole (26.03 mg, 0.2 mmol) were added into a 10 mL pear-shaped bottle, vacuumed and filled with argon. 2 mL anhydrous and anaerobic dichloromethane was added into the product **P5** under argon atmosphere, then the solution was added into the pear-shaped bottle filled with DNA under argon atmosphere and sonicated for one minute. The mixture was allowed to stand overnight under argon atmosphere. After the reaction, it was washed with dichloromethane, acetonitrile and oxidized with I_2/THF/Py for 2 minutes, then washed with acetonitrile until the supernatant was colorless. Finally, the CPG-attached oligodeoxynucleotide was cleaved by concentrated ammonia solution in 55 °C for 3 h.

2.2 Characterization of D18–PDIiol Amphiphiles

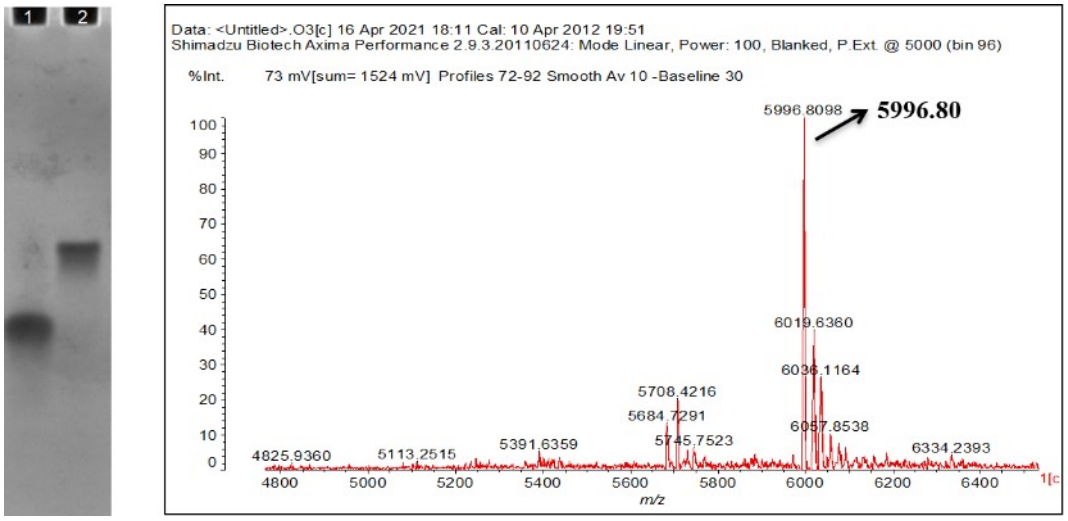


Figure S2. Left: characterization of D18-PDIiol conjugates by 20% denaturing PAGE. Lane 1: D18, Lane 2: D18–PDIiol conjugates. Right: characterization of D18–PDIiol conjugates by MALDI-TOF mass spectrometer and the molecular weight was found to be 5996.80 (Calculated: 5988.12 m/z).

3. Self-Assembly of D18–PDIiol Amphiphiles at Different Conditions

3.1 The self-assembly behavior of of D18–PDIiol through the Addition of different solvents

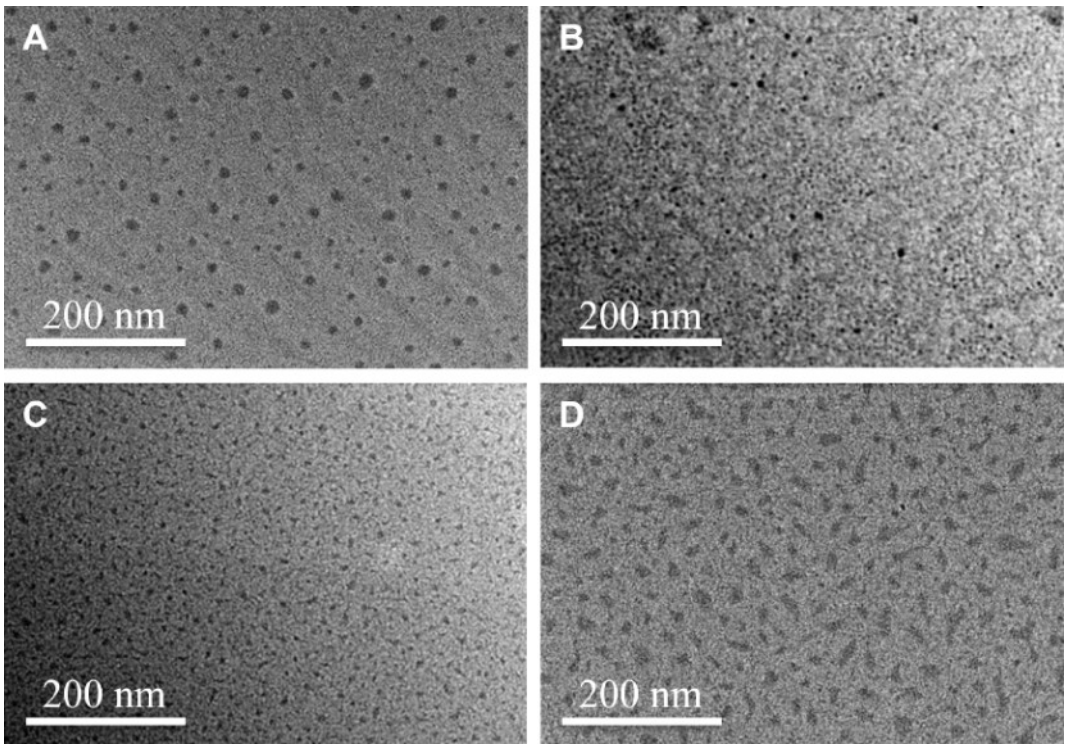


Figure S3. TEM images of D18–PDIiol amphiphiles at different conditions. (A) THF/H_2O, v/v, 1:20, (B) DCM/ H_2O, v/v, 1:20, (C) CH_3CN/ H_2O, v/v, 1:20 and (D) THF/ H_2O, v/v, 1:10.

3.2 The CMC of D18–PDIiol conjugates

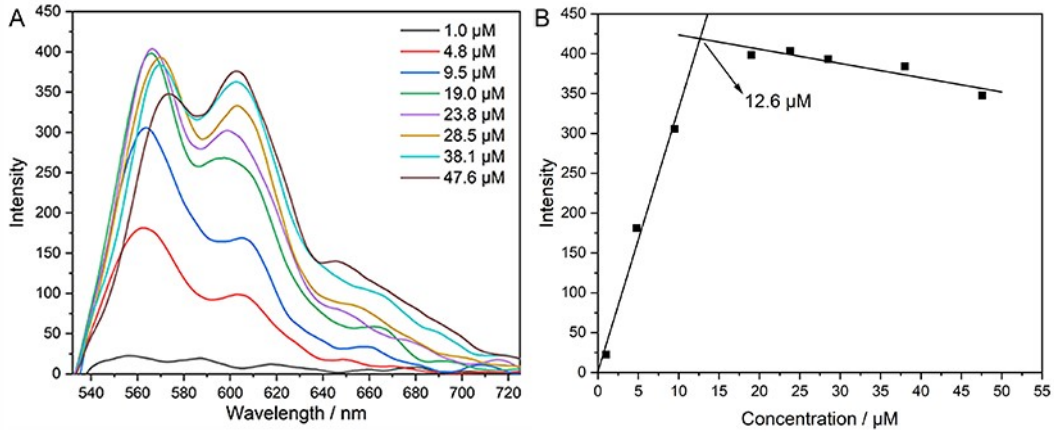


Figure S4. (A) Fluorescence spectra of D18–PDIiol assemblies at different concentrations. (B) Determination of the critical micelle formation concentration (CMC) of D18–PDIiol and the fluorescence intensity of PDI as a function of the concentration of D18–PDIiol.

4. Morphology Regulation of D18–PDIiol through Host–Guest Interaction

4.1 Morphology Regulation of D18–PDIiol through Addition of β-CD

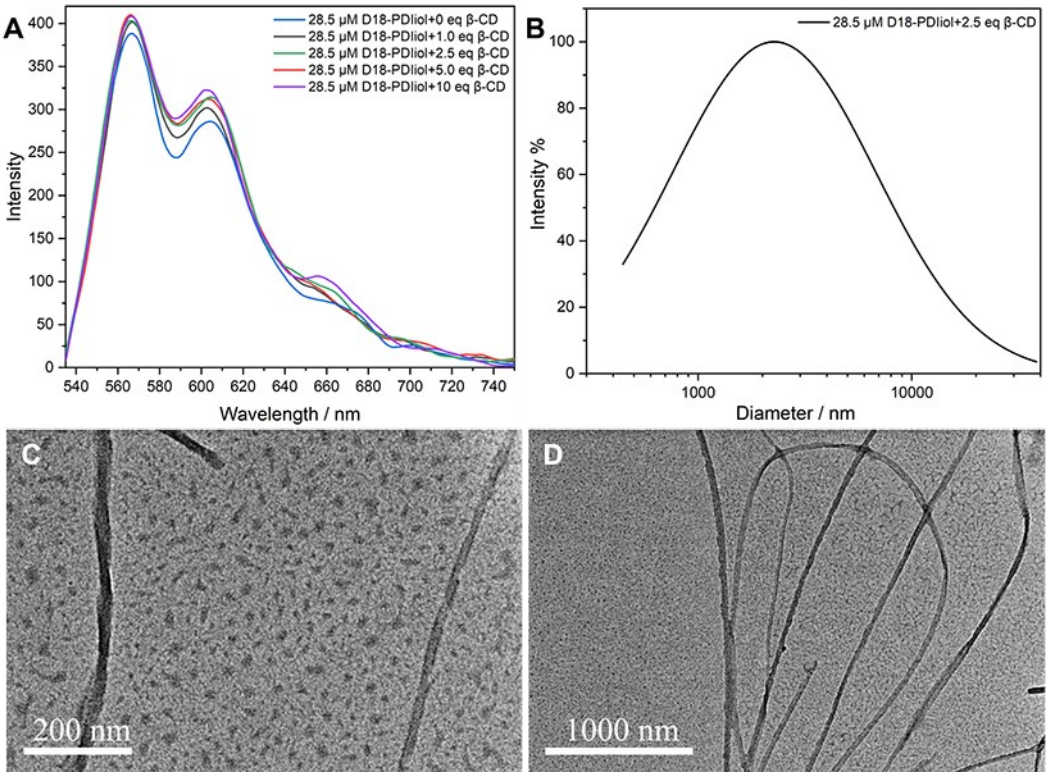


Figure S5. (A) Fluorescence spectra of D18-PDIiol upon addition of different equivalent β-CD. (B) DLS size distribution of the assembled D18–PDIiol micelles with the addition of 2.5 equivalent of β-CD. (C and D) TEM images of assembled D18–PDIiol micelles with the addition of 1 equiv. β-CD. (Annealing process: The sample was heated to 90 °C and maintained for 30 min, then cooled slowly to room temperature and maintained overnight.)

4.2 Morphology Regulation of D18–PDIiol Assemblies through Addition of α-CD

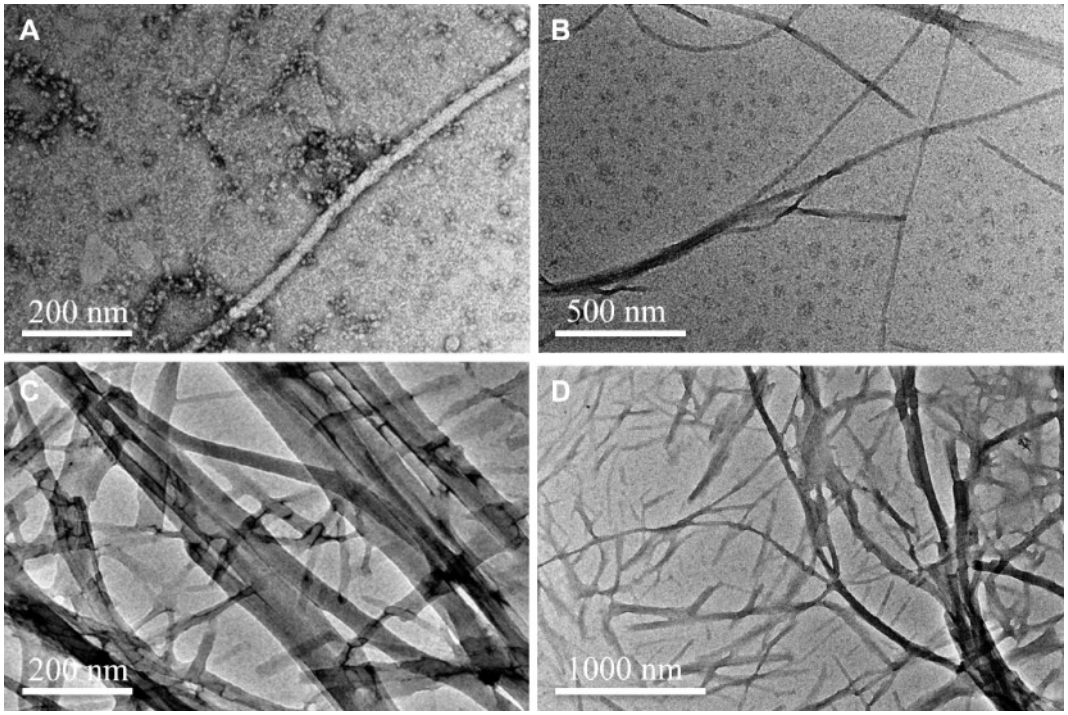


Figure S6. TEM images of assembled D18–PDIiol micelles with the addition of 1 equiv. α-CD (A, B) and 2.5 equiv.α-CD (C, D). (Annealing process: The sample was heated to 90 °C and maintained for 30 min, then cooled slowly to room temperature and maintained overnight.)

5. The Reversible Transformation of the Assemblies

5.1 Fluorescence spectra of D18–PDIiol, D18-PDIiol@β-CD and D18-PDIiol@β-CD with the addition of AMA

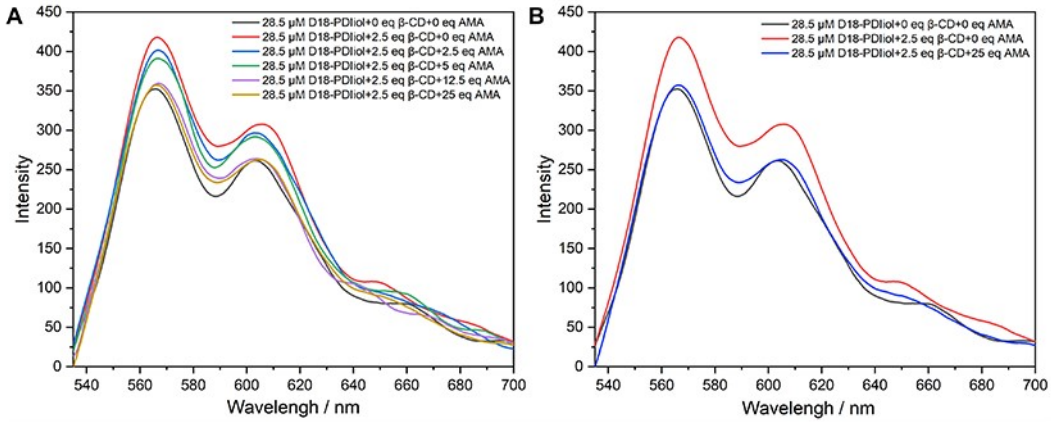


Figure S7 (A) Fluorescence spectra of D18-PDIiol, D18-PDIiol@β-CD and D18–PDIiol@β-CD with the addition of different equivalent AMA. (B) Fluorescence spectra of D18-PDIiol, D18-PDIiol@β-CD and D18–PDIiol@β-CD+25 equivalent of AMA.

5.2 D18–PDIiol@β-CD nanofibers with the addition of AMA (25 equiv.) and maintained at room temperature overnight

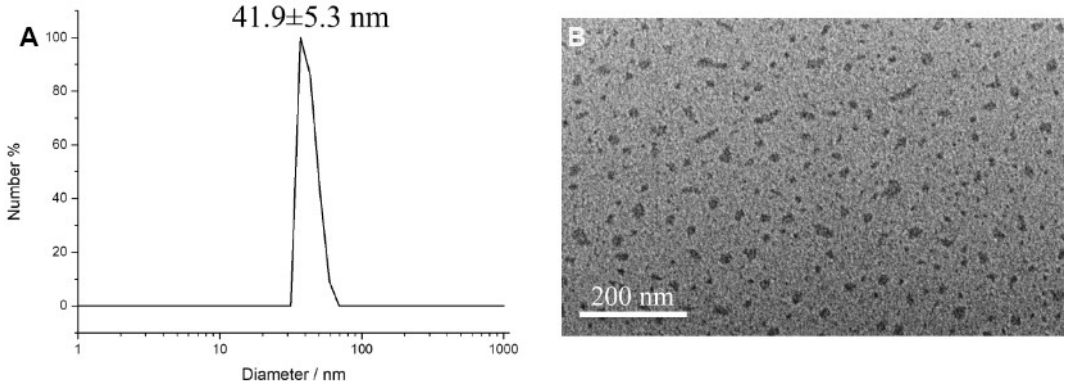


Figure S8. DLS size distribution (A) and TEM image (B) of 28.5 μM D18–PDIiol@β-CD nanofibers with the addition of AMA (25 equiv.).

5.3 D18–PDIiol assemblies with the addition of AMA (25 equiv.).

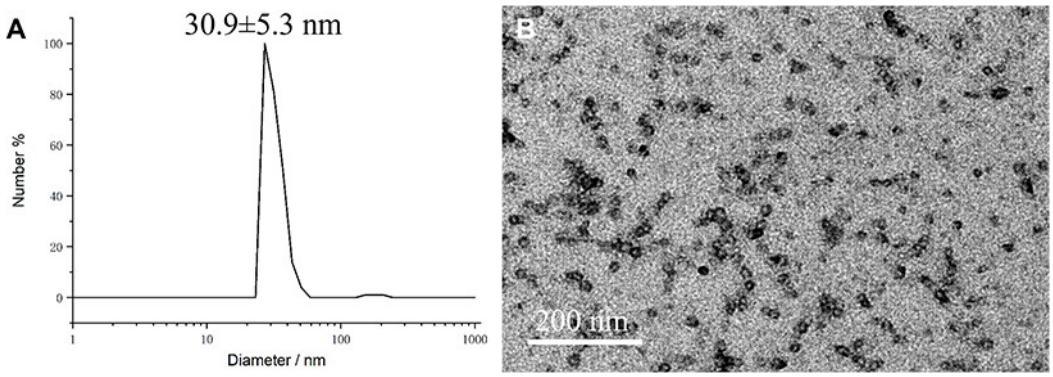


Figure S9. DLS size distribution (A) and TEM image (B) of 28.5 μM D18–PDIiol assemblies with the addition of AMA (25 equiv.).

6. Characterization of 5 nm Gold Nanoparticles Decorated on Assemblies

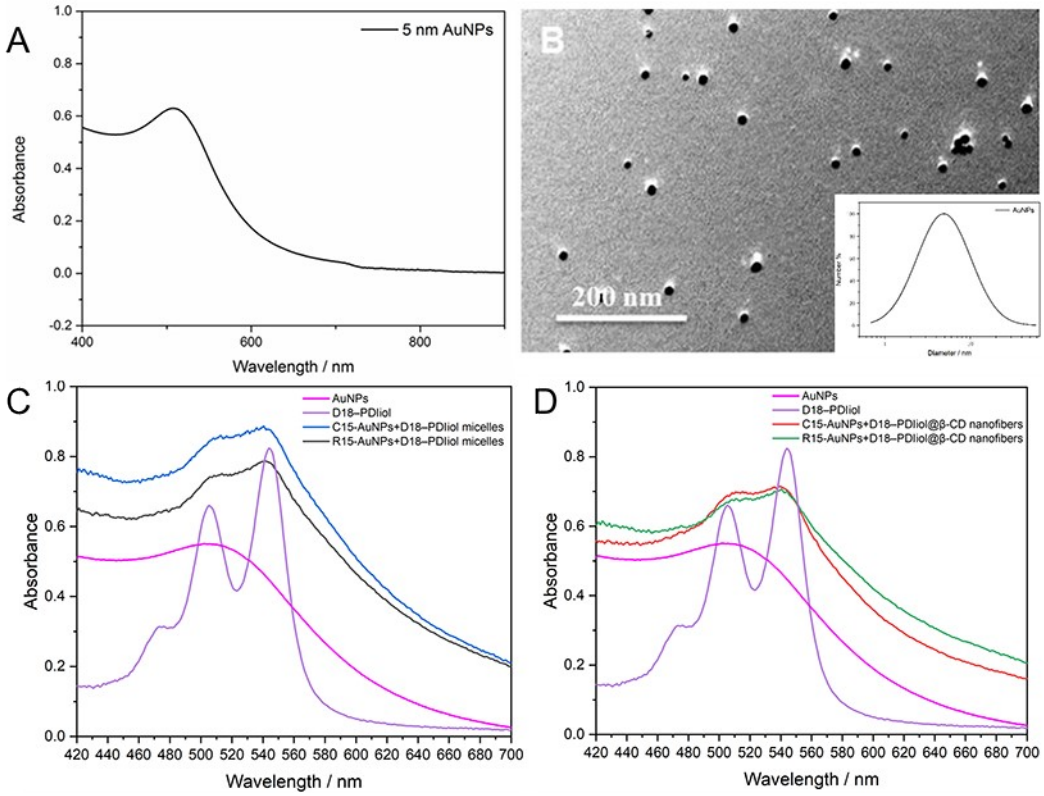


Figure S10. (A) UV-Vis absorption spectral of 5 nm AuNPs. (B) TEM image of 5 nm AuNPs. Inset: DLS size distribution of 5 nm AuNPs. (C) UV-Vis absorption spectral of 5 nm AuNPs, D18-PDIiol, complementary DNA(D15) modified AuNPs with D18–PDIiol micelles and non-complementary DNA(R15) modified AuNPs with D18–PDIiol micelles. (D) UV-Vis absorption spectral of 5 nm AuNPs, D18-PDIiol, complementary DNA(D15) modified AuNPs with D18–PDIiol@β-CD nanofibers and non-complementary DNA(R15) modified AuNPs with D18–PDIiol@β-CD nanofibers.

Reference

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2 (*a*) A. V. Azhayev, M. L. Antopolsky, *Tetrahedron* 2001, **57**, 4977–4986; (*b*) C. H. Wohlgamuth, M. A. McWilliams, A. Mazaheripour, A. M. Burke, K.-Y. Lin, L. Doan, J. D. Slinker, A. A. Gorodetsky, *J. Phys. Chem. C* 2014, **118**, 29084–29090.

3 F. Menacher, V. Stepanenko, F. Wurthner, H. A. Wagenknecht, *Chem. Eur. J.* 2011, **17**, 6683–6688.