

Supporting Information

Reversible morphology tuning of DNA-perylenebisdiimide assemblies through 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, N, N-Dimethylethylenediamine and 3-Propargyl bromide were purchased from Aladdin. All of the DNA sequence was obtained from IDOBIO Company (Beijing, China). CB[8], CB[10]¹ and PDI² were prepared by the corresponding literature procedures. The water used in all of the experiments was Milli-Q deionized (18.2 M Ω .cm).

DNA sequence:

DNA: 5'-N₃-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.

TEM measurements: The sample was applied to a carbon grid by adding a 7 μ L drop of sample solution to the grid and carefully removing it after 45 s immersion using a filter paper. The grid was allowed to dry for at least 15 min before applying 7 μ L of a 1 wt% uranyl acetate aqueous solution, which was removed after 20 s. The grid was again allowed to dry for at least 15 min. Samples were studied on a JEOL JEM-2100 TEM (Jeol, Japan).

Dynamic Light Scattering (DLS) experiments: The experiments were performed on Nicomp 380 Z3000.

Atomic Force Microscope (AFM) analyses: The experiments were carried out on Keysight SPM6500. Samples were prepared by drop casting 10 μ L solution of the sample on freshly cleaved mica surface and dried under air. Imaging was done under ambient condition in tapping mode. The probe used was antimony doped silicon cantilever with a resonant frequency of 300 kHz and spring constant of 40 Nm⁻¹.

Fluorescence measurements: The experiments were conducted using a PerkinElmer SL-55 Fluorescence Spectrometer.

UV/Vis measurements: The experiments were performed on a SHIMADZU UV-3600

instrument with 1 cm pathlength cells at 298 K.

¹H NMR measurements: All ¹H NMR spectra were collected on Agilent 600 MHz DD2.

Fluorescence microscopic measurements: Sample for FE-SEM was prepared by drop 7 μ L of the sample onto a clean coverslip and covered by a second one. The DNA solution was drawn under the capillary forces created by the two slides and sealed with vacuum grease. Samples were imaged on FLUOVIEW FV3000. 505 nm was used as excitation wavelength and images were recorded using the corresponding software (FV31S-SW).

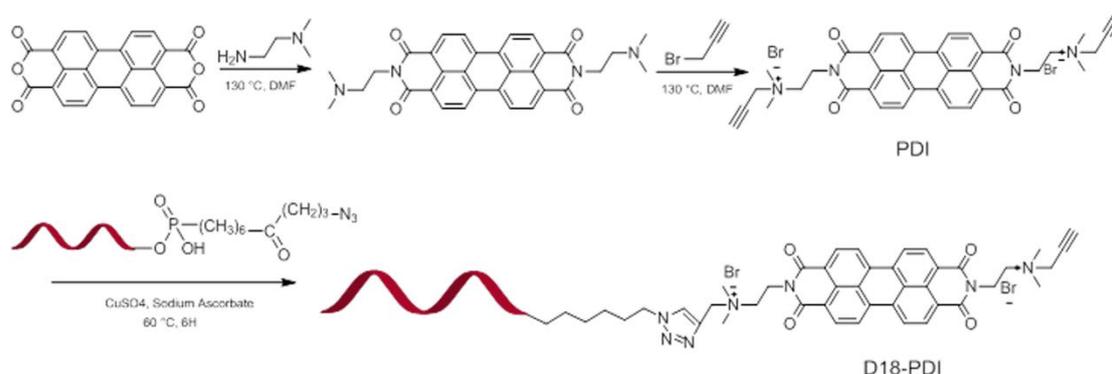
General procedure for preparation of DNA modified AuNPs solution³:

A solution of DNA (50 μ M, 12 μ L) was added into the 13 nm AuNPs (18.8 nM, 100 μ L) pH 7.5, 0.1 \times TBE buffer with 20 mM NaCl solution. The mixed solution were incubated at room temperature overnight and then centrifugation at 13 000 rpm for 45 min to remove excess reagents. After remove the supernatant, the red precipitate was washed twice with pH 7.5, 0.1 \times TBE buffer with 20 mM NaCl by successive centrifugation and redispersion and then finally redispersed in 10 μ L fresh pH 7.5, 20 mM NaCl, 0.1 \times TBE buffer.

Hybridization process:

188 nM (3 μ L) DNA modified AuNPs and 30 μ M D18-PDI/CB[10] solution (10 μ L) were incubated in 0.1 \times TBE (pH 7.5) and 20 mM NaCl at room temperature overnight.

2. Synthesis and Characterization of D18-PDI conjugates



Scheme S1 Synthetic route of D18-PDI conjugates

- (1) PDI was synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride in two steps with high yield following the previous literatures.^{2a}
- (2) **Procedure for the preparation of D18-PDI conjugates^{2b}**: a solution of N₃-D18 (0.33 mM, 100 nmol) in H₂O (300 μL) were added DMF (60 μL), PDI (50 mM in H₂O, 400 nmol, 8 μL), freshly prepared aq CuSO_4 (40 mM, 400 nmol, 10 μL) and sodium ascorbate (100 mM, 2 μmol , 20 μL). The reaction mixture was allowed to stay $60\text{ }^\circ\text{C}$ for 6 hrs. Then the product was purified by 20% denaturing polyacrylamide gel electrophoresis (PAGE) with $1 \times$ TBE buffer as the running buffer. The identification of the conjugates was achieved by UV shadowing. The respective bands were excised from the gel and incubated in deionized water for 24 hrs. After centrifugation, the supernatant was desalted with C18 column and dried by speed vacuum concentrator. The purity of D18-PDI was assessed by 20% PAGE, followed by staining with Stains All. The samples were stored at $-20\text{ }^\circ\text{C}$ before use. The products were analyzed by MALDI-TOF.

MALDI-TOF MS: D18-PDI 6262.0 m/z

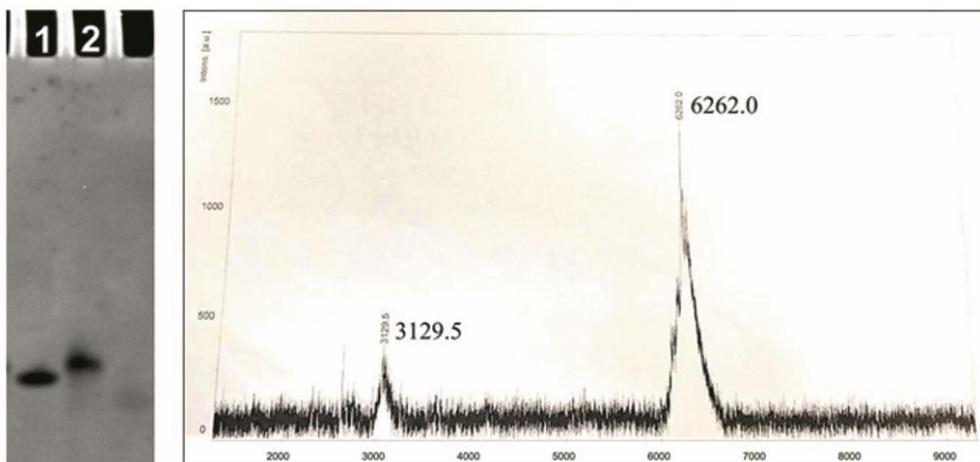


Fig. S1 Left: characterization of DNA-PDI conjugates by 20% denative PAGE, lane 1: azide modified D18, lane 2: D18-PDI conjugates. Right: characterization of D18-PDI conjugates by MALDI-TOF mass spectrometer and the molecular weight was found to be 6262.0 (Calculated: 6267 m/z).

(3) **Addition of CB[n] to the solution of D18-PDI conjugates:** Due to the poor solubility of CB[8] and CB[10], we added suspension solution (1.3 mM CB[8] or 2.0 mM CB[10]) to the assembled solution of D18-PDI conjugates in proportion, to avoid the change of the concentration of assemblies.

3. Fluorescence spectra of D18-PDI with addition of CB[8]

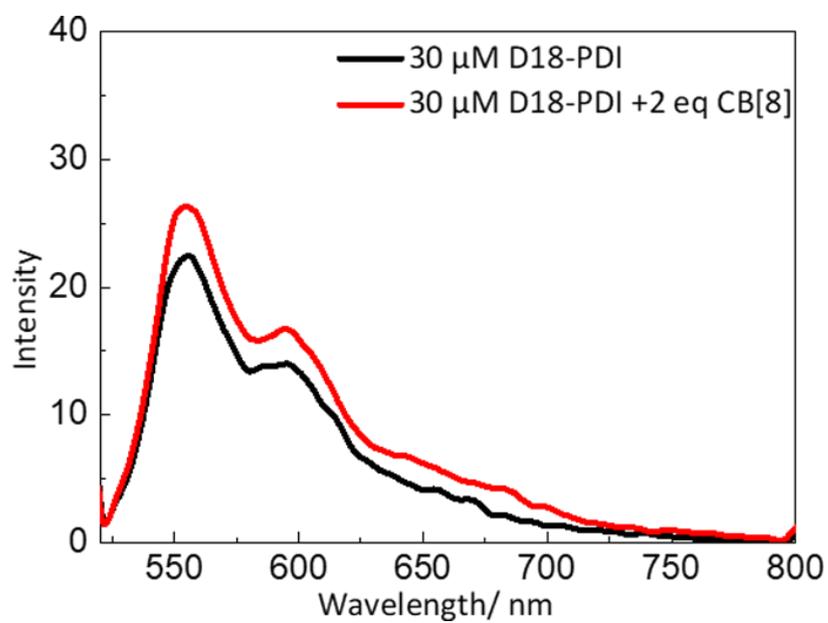


Fig. S2. Fluorescence spectra for D18-PDI upon addition of 2 equiv. CB[8] (Annealing process: heat to 90 °C and stay 30 min, then cool slowly to room temperature and stay overnight).

4. TEM tests of D18-PDI/CB[10] at different conditions

(1) Condition: stay overnight at room temperature.

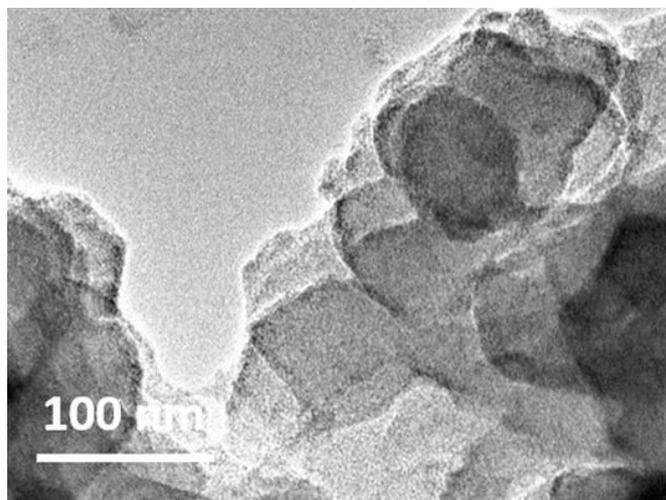


Fig. S3. TEM images of 30 μM D18-PDI with the addition of CB[10].

(2) Condition: mixed solution of 30 μM D18-PDI and CB[10] under the condition of heat to 90 °C and stay 30 min, then cool slowly to room temperature and stay overnight.

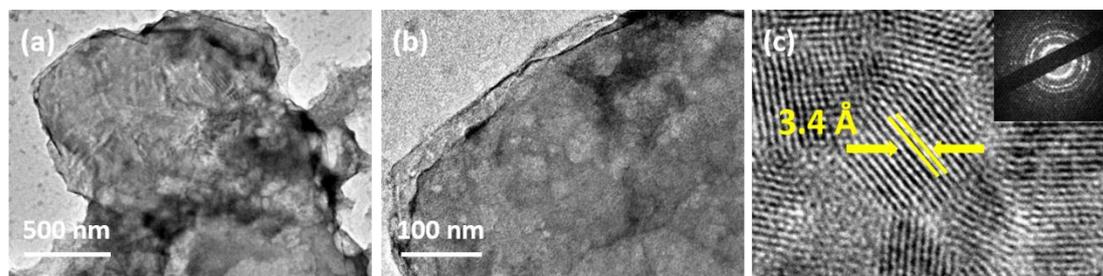


Fig. S4. (a) and (b) TEM images of directly assembling of 30 μM D18-PDI and CB[10] mixed solution under the annealing condition. (c) HR-TEM images of DNA sheets. The insets of (c) shows the SAED pattern of DNA sheets.

5. UV/Vis and Fluorescence spectra of D18-PDI with the addition of CB[10]

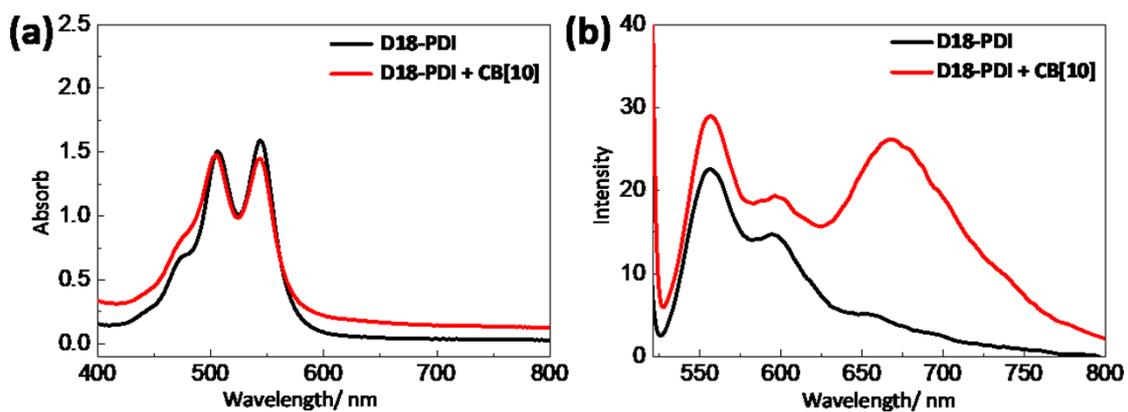


Fig. S5. (a) UV/Vis absorption spectral changes of assembled 30 μ M D18-PDI micelles with the addition of CB[10]. (b) Emission spectral changes of assembled 30 μ M D18-PDI micelles with the addition of CB[10] ($\lambda_{\text{ex}} = 505$ nm).

6. ^1H NMR, UV/Vis, ESI-MS and Fluorescence spectra of PDI with addition of CB[10]

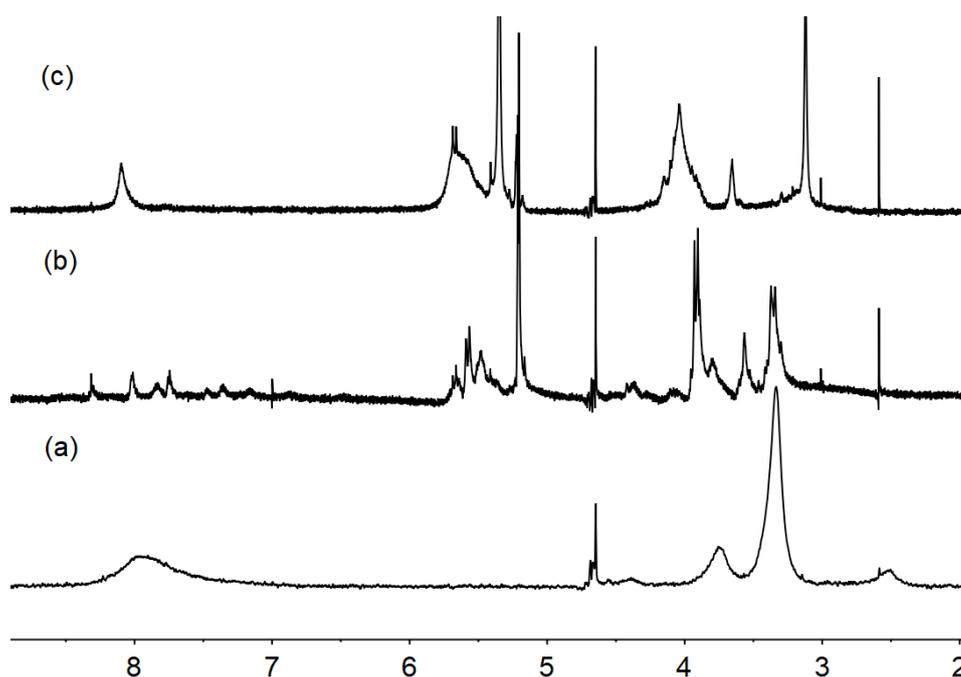


Fig. S6. ^1H NMR spectra (600 MHz, D_2O , 298 K) of PDI (0.5 mM) in the presence of CB[10], a) 0 eq, b) 0.5 eq, c) 1 eq. The encapsulation of hydrophobic moieties inside the CB[10] cavity usually leads to a upfield shift whereas deaggregation of PDI units is known to result in a downfield shift. Due to the poor solubility of CB[10] in water, excess CB[10] as solid was added to the solution of PDI guest and integration shows that CB[10] is about 1 equivalent in c).

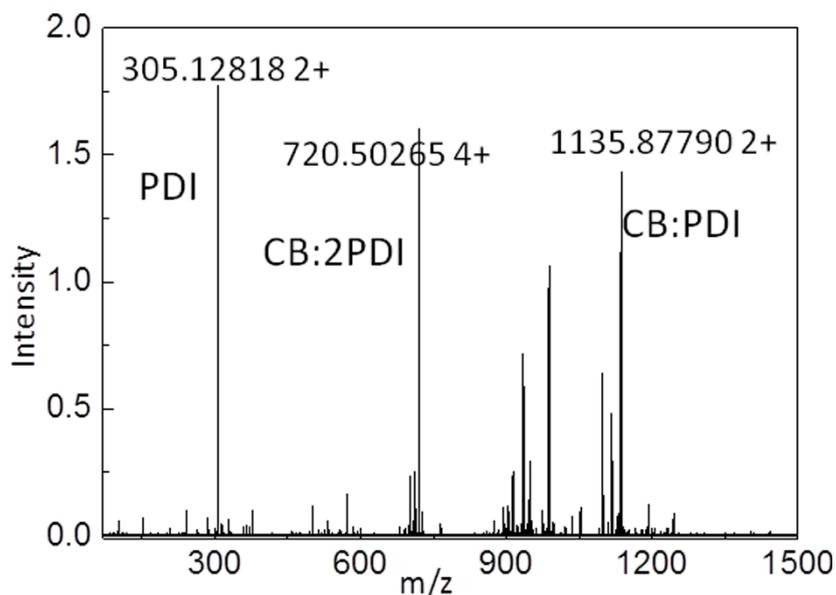


Fig. S7. ESI-MS spectrum of PDI with CB[10] (The ion at $m/z = 305.1$ corresponding to the guest molecule ($\text{PDI}^{2+} = 305.1$); ion at $m/z = 1135.8$ corresponding to the 1:1 host-guest complex ($[\text{CB}[10]+\text{PDI}^{2+}]^{2+} = 1135.8$), ion at $m/z = 720.5$ corresponding to the 1:2 host-guest complex ($[\text{CB}[10]+2\text{PDI}^{2+}]^{4+} = 720.5$)).

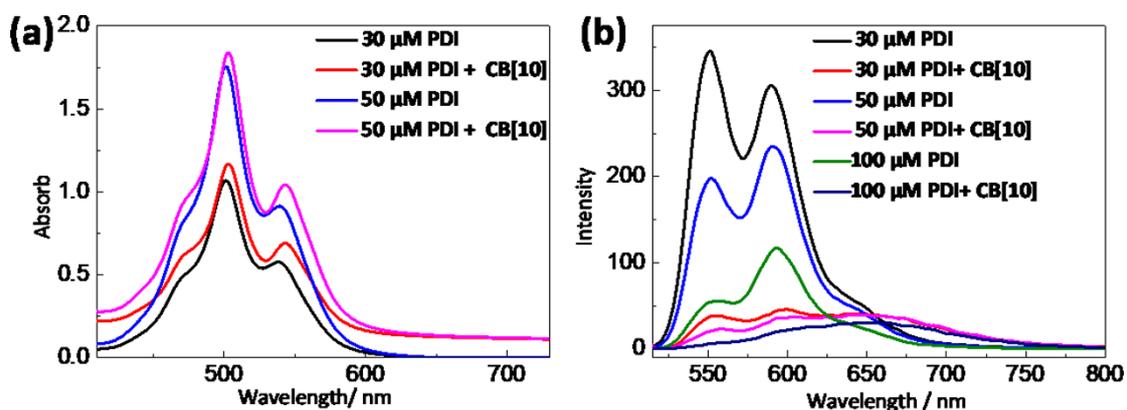


Fig. S8. (a) UV/Vis spectra of PDI units with addition of CB[10]. (b) Fluorescence spectra for different concentrations of PDI units upon addition of CB[10].

7. TEM test and Fluorescence spectra of DNA nanosheets with addition of DMAMA

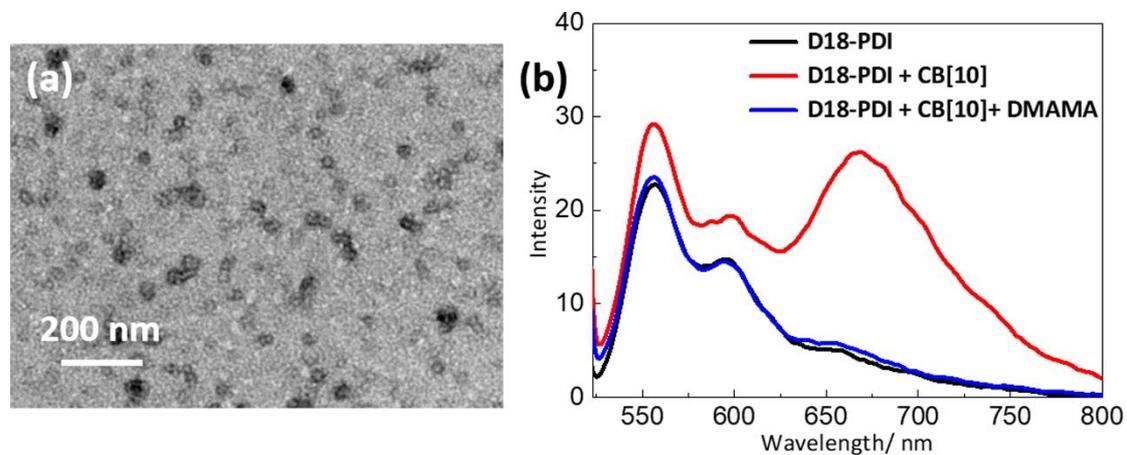


Figure. S9. (a) TEM images of DNA nanosheets after adding 20 equiv. **DMAMA** (10 mM) solution. (b) Emission spectral changes of D18-PDI micelles with the addition of excess CB[10] and then adding 20 equiv. **DMAMA** (10 mM) (Annealing process: heat to 90 °C and stay 30 min, then cool slowly to room temperature and stay overnight).

References:

1. (a) A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094–8100. (b) X. Yang, Z. Zhao, X. Zhang and S. Liu, *Sci. China Chem.*, 2018, **61**, 787-791.
2. (a) F. Biedermann, E. Elmalem, I. Ghosh, W. M. Nau and O. A. Scherman, *Angew. Chem. Int. Ed.*, 2012, **51**, 7739-7743. (b) S. Estalayo-Adrià, R. Lartia, A. Meyer, J.-J. Vasseur, F. Morvan and E. Defrancq, *ChemistryOpen*, 2015, **4**, 169-173.
3. Z. Zhao, C. Chen, Y. Dong, Z. Yang, Q.-H. Fan and D. Liu, *Angew. Chem. Int. Ed.* 2014, **53**, 13468-13470.