

## Supporting Information

### **Reversibly Controlled Morphology Transformation of Amphiphilic DNA-dendron Hybrid**

**Liying Wang,<sup>a</sup> Yu Feng,<sup>a</sup> Zhongqiang Yang,<sup>b</sup> Yan-Mei He,<sup>a</sup> Qing-Hua Fan,<sup>\*a</sup> and  
Dongsheng Liu<sup>\*b</sup>**

<sup>a</sup> *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry and Graduate School, the Chinese Academy of Sciences, Beijing 100190, China.*

*E-mail: [fanqh@iccas.ac.cn](mailto:fanqh@iccas.ac.cn)*

<sup>b</sup> *Optoelectronics & Molecular Engineering of the Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China.*

*E-mail: [liudongsheng@tsinghua.edu.cn](mailto:liudongsheng@tsinghua.edu.cn)*

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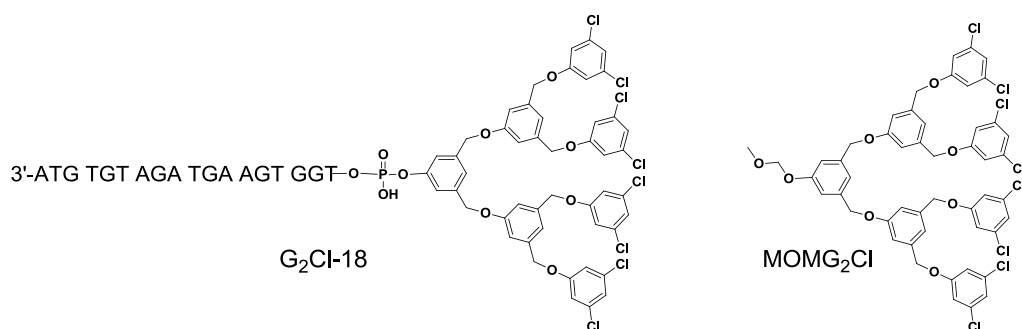
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## 1. General Information

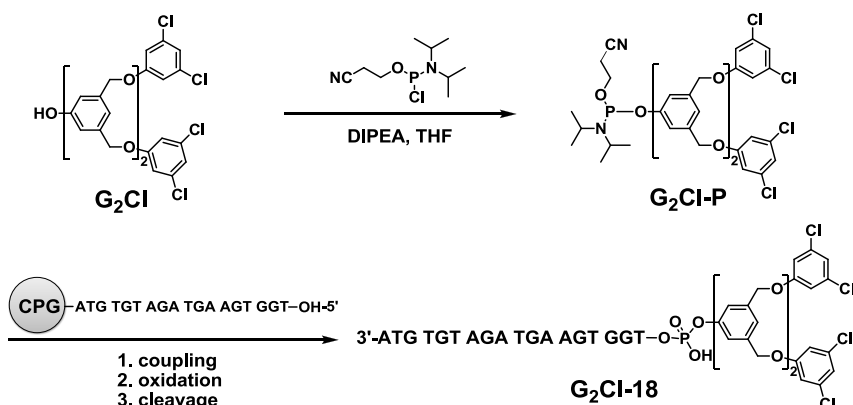
Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques. Matrix-assisted laser desorption-ionization (time of flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer with  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA) as the matrix.  $^1\text{H}$  NMR was performed on a 400 MHz Avance NMR spectrometer (Bruker). The XRD patterns were obtained by using a Bruker D8 Advance Instrument with Cu K $\alpha$  radiation ( $\lambda=1.5405\text{ \AA}$ ).

All chemicals were obtained from Aldrich or Alfa Aesar (Tianjing, China) and used as received unless otherwise mentioned. The organic solvents used for synthesis were dried according to published methods.<sup>1</sup> Water used in all experiments was Milli-Q deionized (15.6 M $\Omega$ .cm).

## 2. Synthesis of DNA-Dendron Hybrid



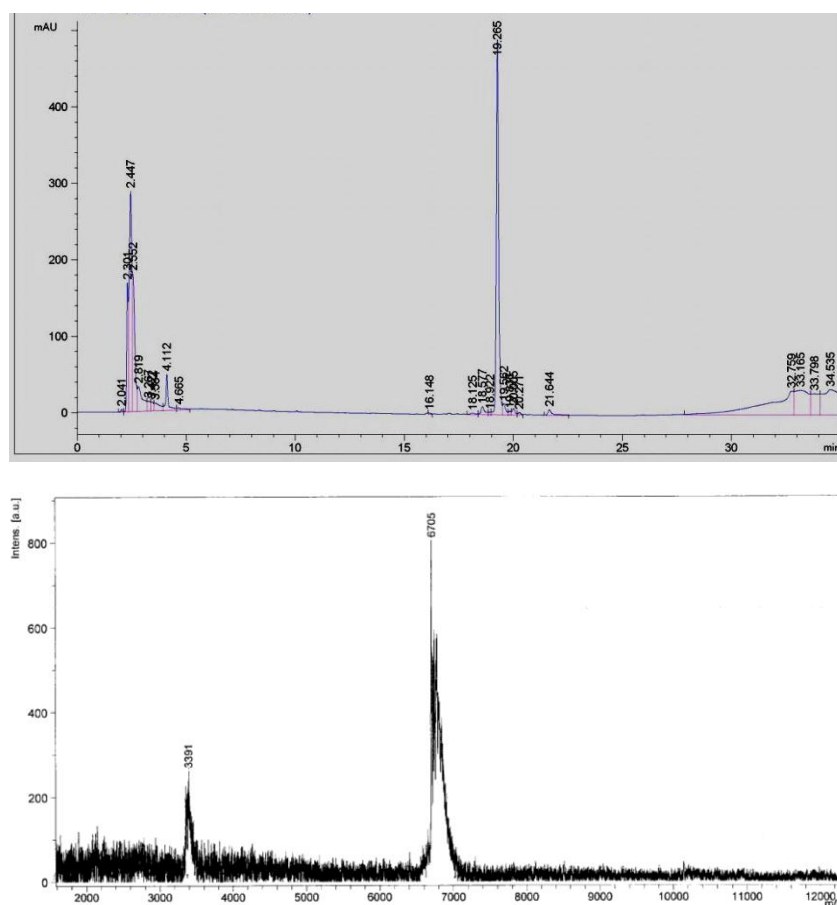
**Scheme S1.** Chemical structures of G<sub>2</sub>Cl-18 and MOMG<sub>2</sub>Cl



**Scheme S2.** The solid phase synthesis of G<sub>2</sub>Cl-18 hybrid

Dendron G<sub>2</sub>Cl was synthesized using the repetitive ester reduction and Mitsunobu reaction as described previously.<sup>2</sup> G<sub>2</sub>Cl was conjugated with the 18mer DNA using the solid-phase synthetic method.<sup>2</sup> Briefly, The DNA-loaded CPG (1 μmol) was transferred into a vial, then 5-ethylthiotetrazole (100 μmol) and G<sub>n</sub>Cl-P (50 μmol) were added consequently. After dried *in vacuo*, 0.5 mL anhydrous THF was added under nitrogen protection. The reaction mixture was allowed to stay overnight under room temperature. Then CPG was washed twice with anhydrous THF followed by oxidation with iodine and water in THF. After cleaved by concentrated ammonia solution at 55 °C for 3 h, the crude product was purified by HPLC using a C4 column, the product was eluted as a single sharp peak and was well-separated from the

incomplete short sequences. The retention time for the product is around 20 min. The solvent condition: 100 mM triethylamineacetic acid buffer (TEAA, pH 7.0). Acetonitrile fraction was changed from 10% to 100% in 30 min with the elution rate 1 mL/min. The final product was confirmed by MALDI-TOF spectrum.



**Figure S1.** HPLC profile of G<sub>2</sub>Cl-18 crude product and MALDI-TOF spectrum of the final product.

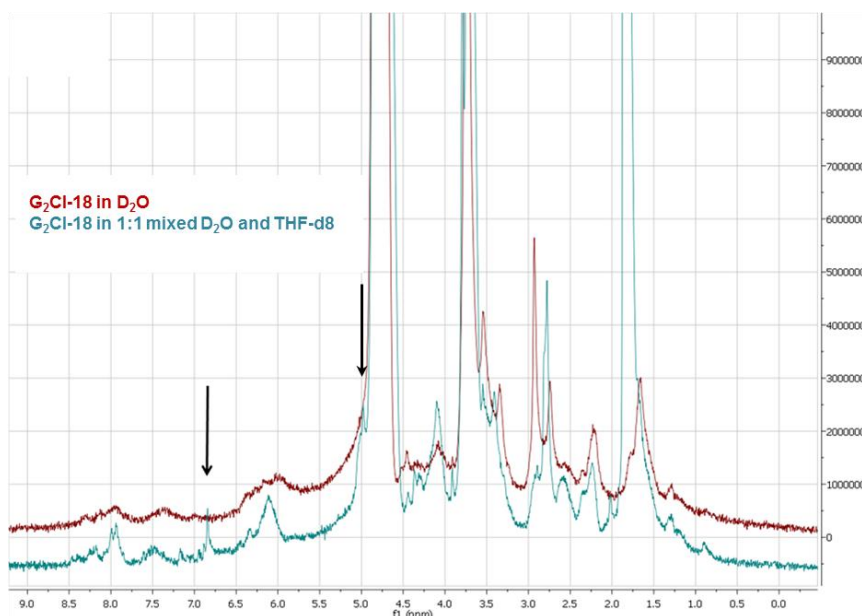
### 3. Formation of Assemblies and Morphology Transformation

**Spherical micelle formation by the dialysis method:** 50  $\mu\text{L}$  THF was added to a 50  $\mu\text{L}$   $\text{G}_2\text{Cl-18}$  stock solution (200  $\mu\text{M}$ ) and stirred for 2 h.  $\text{G}_2\text{Cl-18}$  was dissolved molecularly in this 1:1 mixed solution as confirmed by the  $^1\text{H}$  NMR. 400  $\mu\text{L}$  water was added slowly (5  $\mu\text{L}/\text{min}$ ) under vigorously stirring. The solution was stirred overnight and then dialyzed against water for 24 h and then characterized by DLS and TEM.

**Nanofiber formation method:** The  $\text{G}_2\text{Cl-18}$  was dissolved in water to make a concentration of 20  $\mu\text{M}$ . 5  $\mu\text{L}$  of dichloromethane was added to 100  $\mu\text{L}$   $\text{G}_2\text{Cl-18}$  solution and centrifuged at 6000 rpm/min for 2 min to make the dichloromethane beneath the water phase, the solution was heated to 90  $^\circ\text{C}$  and kept for 30 min, and then allowed to cool to room temperature naturally or at a desired rate. Keep the assembled solution under 4  $^\circ\text{C}$  for storage before used.

**Spherical micelle to nanofiber transformation:** 5  $\mu\text{L}$  of dichloromethane was added to a 100  $\mu\text{L}$   $\text{G}_2\text{Cl-18}$  spherical micelle solution and centrifuged at 6000 rpm/min for 2 min, the solution was heated to 90  $^\circ\text{C}$  and kept for 30 min, and then allowed to cool to room temperature naturally.

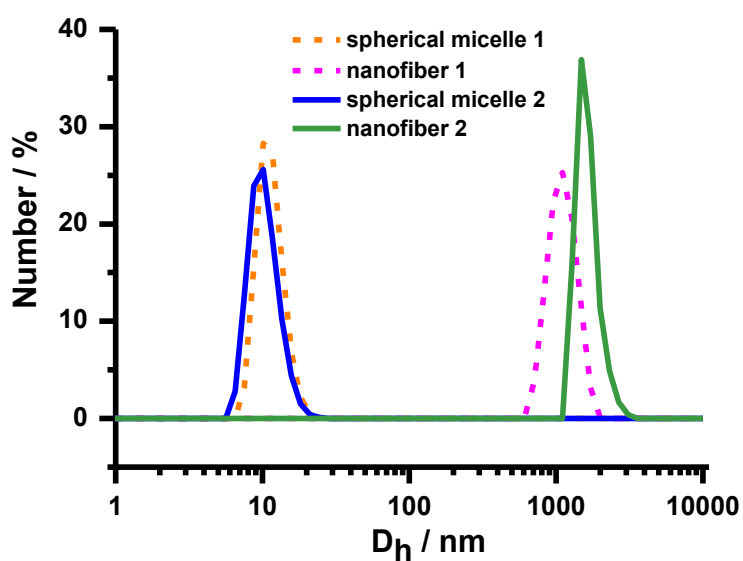
**Nanofiber to spherical micelle transformation:** 10  $\mu\text{L}$  THF was added to 100  $\mu\text{L}$   $\text{G}_2\text{Cl-18}$  nanofiber solution and kept for 2 days under room temperature. Then THF was removed by dialysis against water for 24 h.



**Figure S2.**  $^1\text{H}$  NMR of  $\text{G}_2\text{Cl-18}$  in  $\text{D}_2\text{O}$  and 1:1 mixed  $\text{D}_2\text{O}$  and  $\text{THF-d}_8$ . The arrows point to the peak at 6.8 and 5.0 ppm, which correspond to the hydrogen in the aromatic ring and the methylene group of  $\text{G}_2\text{Cl}$  respectively.

## 4. DLS Results

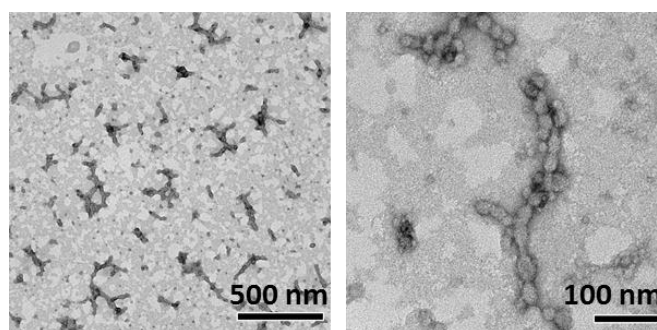
Effective hydrodynamic diameter of the supramolecular system was measured by dynamic light scattering at 25 °C using a dynamic light scattering photometer (Nano ZS ZEN3600, Malvern Instruments Ltd., United Kingdom) equipped with laser at a wavelength of 633 nm.



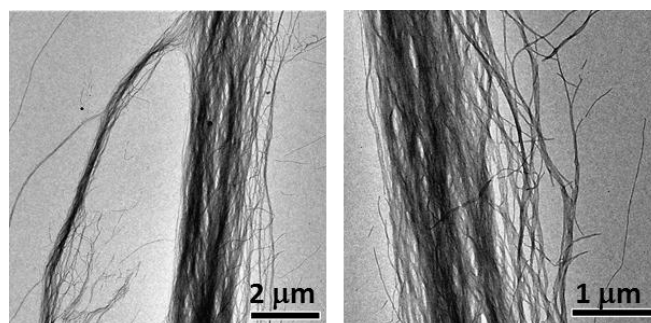
**Figure S3.** The DLS result of the spherical micelles prepared by dialysis method (orange, dashed line) and that of nanofiber after annealing (magenta, dashed line). Spherical micelles reformed after THF addition (blue, solid line) and then nanofibers also reformed after annealing (green, solid line).

## 5. TEM Results

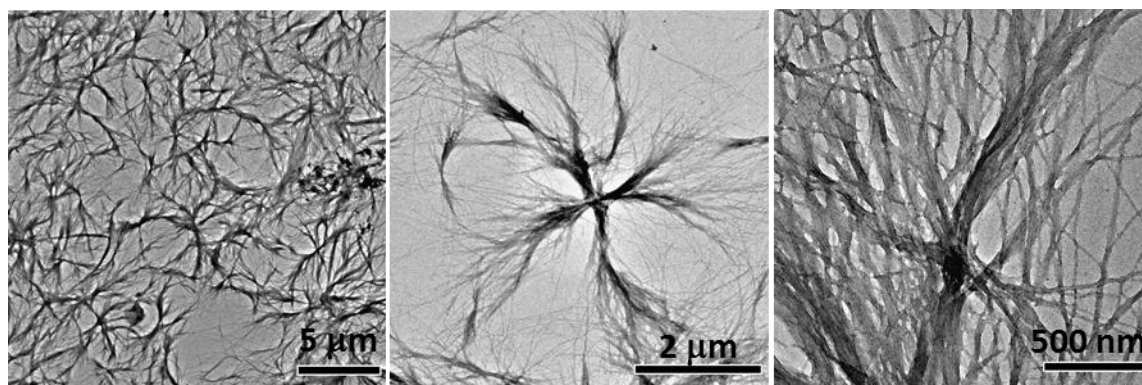
TEM samples were prepared by drop casting 7  $\mu\text{L}$  solution on carbon coated copper grids. After 5 min, the excessive solution was blotted with a piece of filter paper. Then a drop of 1 wt % uranyl acetate aqueous solution was deposited onto the surface of the sample-loaded grid. After 5 min, the excess uranyl acetate aqueous solution was blotted with a piece of filter paper. The sample-loaded grid was dried overnight. TEM images were recorded on a JEOL JEM-1011 microscope operated at 100 KeV.



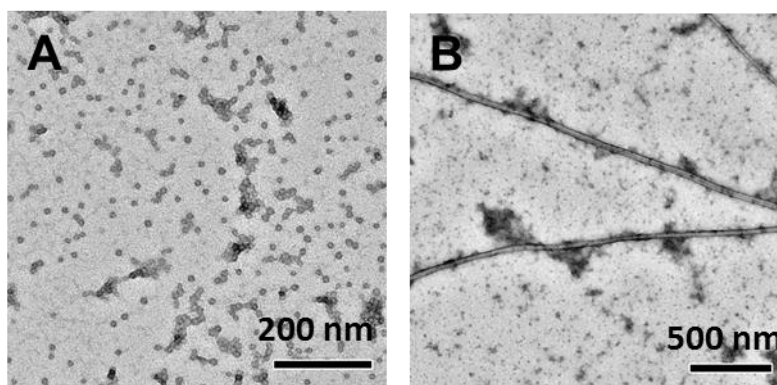
**Figure S4.** TEM images of the intermediate state when the nanofibers transform into spherical micelles.



**Figure S5.** TEM images of nanofibers when  $\text{G}_2\text{Cl-18}$  was slowly cooled at a rate of  $1.5^\circ\text{C} / \text{h}$  after heating at  $90^\circ\text{C}$  for 30 min.



**Figure S6.** TEM images of flower-like aggregates when G<sub>2</sub>Cl-18 was rapidly cooled in an ice bath after heating.

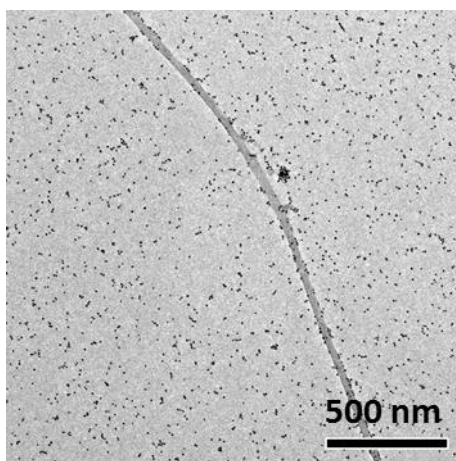


**Figure S7.** TEM images of G<sub>2</sub>Cl-18 at 1:10 mixed THF and water solution after heating the solution to 90 °C for 30 min and cooled to room temperature naturally. Spherical micelles (A) and long nanofibers (B) coexist under this condition.

## 6. DNA-Gold Nanoparticle Conjugates and Hybridization

5 nm gold nanoparticles (AuNPs) and thioctic acid modified DNA were prepared according to the published method.<sup>3</sup> 28.6  $\mu\text{L}$  of DNA (87.4  $\mu\text{M}$ ) was added to 50  $\mu\text{L}$  solution of AuNPs (3.4  $\mu\text{M}$ ). The solution was vibrated overnight at room temperature on an orbital shaker at low speed. Then add 12  $\mu\text{L}$  of 1M NaCl and 3  $\mu\text{L}$  0.4 M phosphate buffer and shake at low speed for another 12 hrs at room temperature. Use ultracentrifuge to centrifuge the suspension to separate the residual DNA strands with the gold nanoparticles. The concentration of the DNA-AuNP conjugates was calculated by measuring the UV absorption of the AuNPs at 520 nm wavelength.

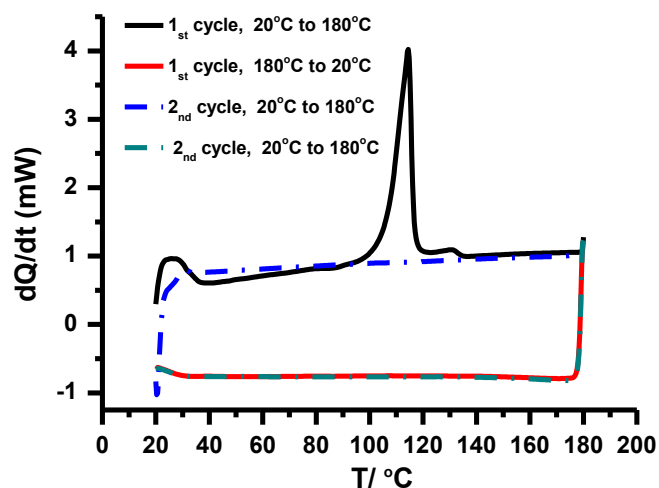
G<sub>2</sub>Cl-18 was first assembled into spherical micelles or nanofibers in 50 mM Tris-HCl buffer at a concentration of 20  $\mu\text{M}$ . Then 5  $\mu\text{L}$  of the assembled solution was mixed and hybridized with 17  $\mu\text{L}$  of the DNA-AuNP conjugates (5.8  $\mu\text{M}$ ) and kept overnight. The solution was characterized by TEM without further treatment.



**Figure S8.** TEM image of G<sub>2</sub>Cl-18 nanofiber mixed with non-complementary (5'-TTTCGCAATGACTGTACT-3') DNA-AuNP conjugates. The AuNPs dispersed randomly, showed no trend of arrangement along the nanofiber.

## 7. DSC Results

DSC was carried out using a METTLER 822e instrument at the range of 20-180 °C and at a heating rate of 10 °C/min. As shown in Figure S9, after melting and cooling cycle, the melting endotherm at 114 °C did not recur during a second, identical heating regime. This experiment was repeated for several times, showing the same phenomenon. The structure of MOMG<sub>2</sub>Cl has no change after the thermo cycle as confirmed by <sup>1</sup>H NMR.



**Figure S9.** DSC melting endotherm of MOMG<sub>2</sub>Cl.

## 8. References

- 1) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals (fifth edition)*; Elsevier Science: USA, **2003**.
- 2) Wang, L.; Feng, Y.; Sun, Y.; Li, Z.; Yang, Z.; He, Y.-M.; Fan, Q.-H.; Liu, D. *Soft Matter* **2011**, 7, 7187-7190.
- 3) Zhang, T.; Chen, P.; Sun, Y.; Xing, Y.; Yang, Y.; Dong, Y.; Xu, L.; Yang, Z.; Liu, D. *Chem. Commun.* **2011**, 47, 5774-5776.