Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Laterally Functionalized Pillar[5]arene: A New Building Block for Covalent Self-assembly

Shuang Fu, Guo An, Hongcheng Sun, Quan Luo, Chunxi Hou, Jiayun Xu, Zeyuan Dong and Junqiu Liu*

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China, Fax: (+86) 0431-8516845

*Email: junqiuliu@jlu.edu.cn

Materials

All the solvents were purchased from Beijing chemical plant. Dichloromethane (DCM), 1, 2-dichloroethane, acetonitrile (MeCN), diethyl ether, chloroform ($CHCl_3$) and tetrachloromethane (CCl_4) were used with further purification. All the reagents were purchased from Energy Chemical plant.

Instruments and methods

^{1}H-NMR spectra was measured by Bruker 510 spectrometer (500 MHz) using chloroform-d ($CDCl_3$) as solvent with tetramethylsilane (TMS) as a reference.

^{13}C-NMR spectra was measured by Bruker 510 spectrometer (600 MHz) using $CDCl_3$ as solvent with TMS as a reference.

Mass spectrometry analysis were performed using liquid chromatograph-mass spectrometer (LC-MS, Agilent1290-micrOTOF-Q Ⅱ) using methanol as solvent.

Fourier transform infrared (FTIR) spectra were recorded on a Vertex 80V spectrometer. The sample was grinded into powder and dried, then mixture with dried KBr (powder) and pressed into piece.

DLS instrument was Malven Instrument zetasizer Nano ZS equipped with a He-Ne laser (633nm, 4mW) and an avalanche photodiode detector.

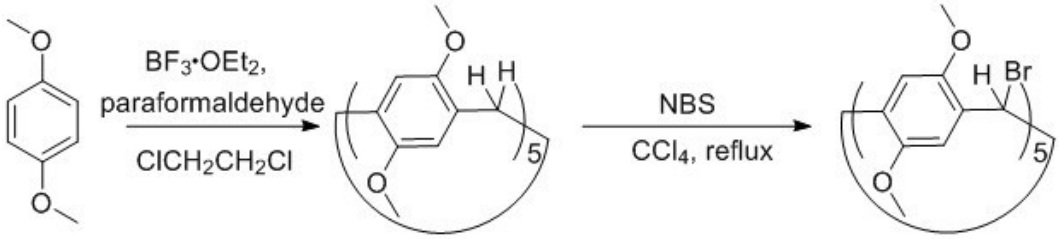
SEM images were recorded on scanning electron microscopy, JEOL JSM 6700F. A drop of the aqueous solution was dripped directly onto a silicon wafer and air-dried.

TEM images were recorded on a JEM-2100F instrument with an accelerating voltage of 200kV. The sample was prepared by placing a drop of the stock solution on a 300-mesh, carboncoated copper grid and air-dried before measurement.

Fluorescence microscope images were charactersized by Olympus BX61. A drop of the sample solution was placed on a colorless piece of glass and air-dried before measurement.

Synthesis of lateral functionalized dimethoxypillar[5]arene (BDMP5)

The synthesis rout of the BDMP5 was shown in scheme S1.



Scheme S1. Synthesis rout of lateral functionalized dimethoxypillar[5]arene (BDMP5).

Synthesis of Dimethoxypillar[5]arene (DMP5): The DMP5 was synthesized according to the previous work.[1] To a solution of 1, 4-dimethoxybenzene (2.79 g, 0.02 mol) in 1, 2-dichloroethane (100 mL), paraformaldehyde (1.96 g) was added under nitrogen atmosphere. The reaction flash was capped and nitrogen bubbled through the solution for 30 min. Then, boron trifluoride diethyl etherate ($BF_3O(C_2H_5)_2$, 1.25 mL, 10 mmol) was added to the solution and the mixture was stirred at room temperature for 3 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The obtained solid was recrystallized from acetonitrile to yield 1.02 g of DMP5 as a white solid. Yield: 34.0%. The ^{1}H-NMR spectrum was shown in Figure S1. 1H-NMR (500 MHz, chloroform-d, 25 °C, TMS): δ (ppm) = 6.84 (S, 10H, phenyl), 3.76 (S, 10H, bridge methylene), 3.71 (s, 30H, methoxy).

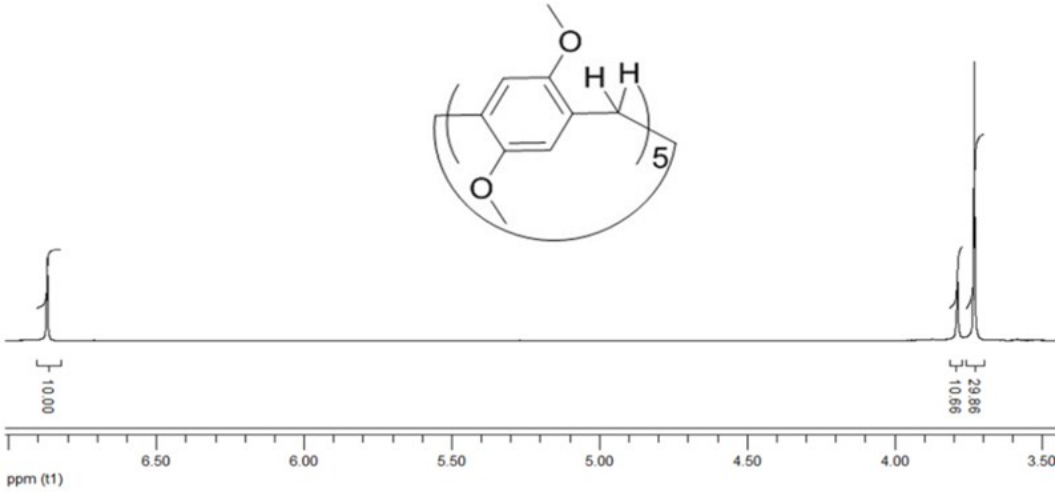


Figure S1. The ^{1}H-NMR (500 MHz, chloroform-d, 25 °C, TMS) spectrum of synthesized DMP5.

Synthesis of BDMP5: The BDMP5 was synthesized by reference of previous work of preparing bromo calix[n]arenes.[2] DMP5 (1.2 g, 1.6 mmol) was taken in a flask and CCl_4 (100 mL) was added. The reaction mixture was refluxed at 70 °C and NBS (1.8 g, 8.9 mmol) was added to it in four stages. After 20 h the reaction was stopped and cooled and then poured into 10% sodium bisulphite solution. The organic layer was separated by extraction. The aqueous mixture was further extracted by dichloromethane. The organic extracts were combined and concentrated. Then the concentrated extracts were precipitated by adding hexane. The solid was separated and recrystallized with $CHCl_3$/CH_3OH to afford the BDMP5 as yellow powder (0.33 g). The BDMP5 has been characterized by ^{13}C-NMR (Figure S3), mass (Figure S2) and FTIR analysis (Figure S4).

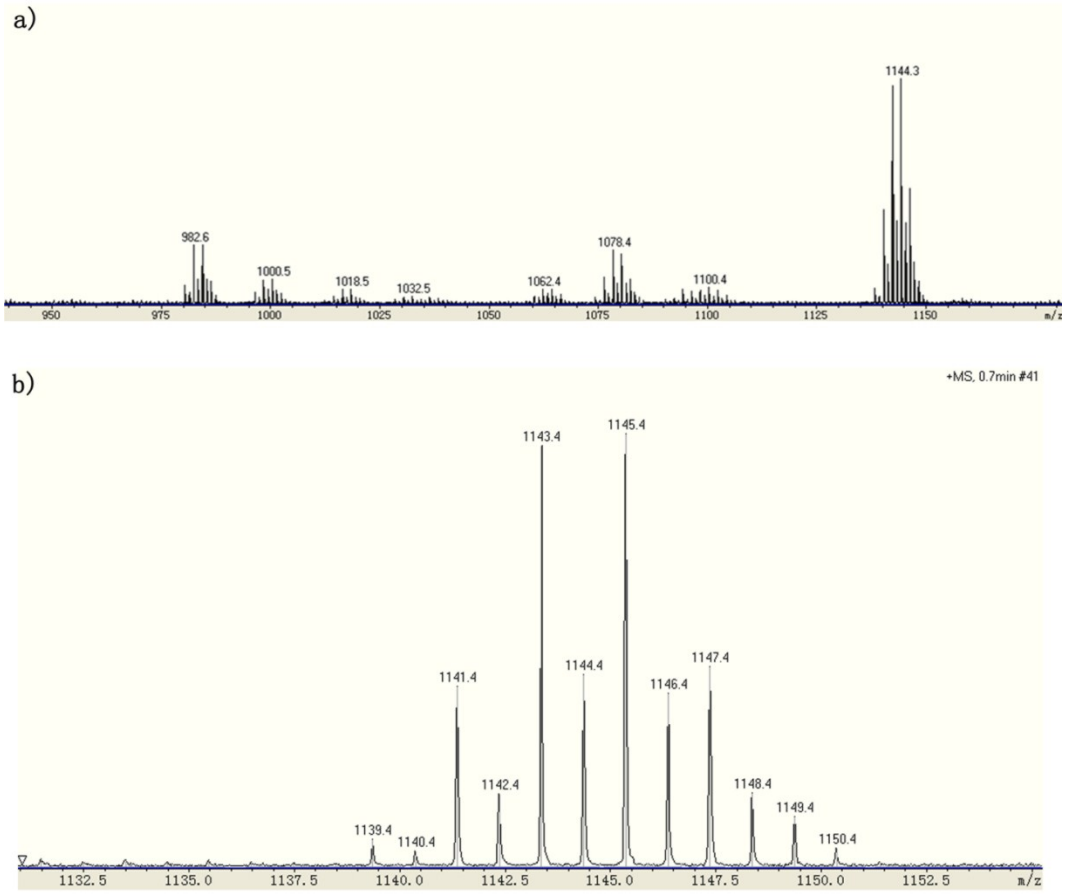


Figure S2. a) ESI-TOF mass spectrum of BDMP5; b) the amplified molecular ion peaks of the fivefold BDMP5 (m/z found 1139.4 (M^+, calculated: 1139.4 for $C_{45}H_{45}O_{10}Br_5$ (79 Br)), 1140.4 ($[M+H]^+$, calculated: 1139.4 for $C_{45}H_{45}O_{10}Br_5$ (79 Br)), 1141.4, 1143.4, 1145.4 1147.4 (M^+, for $C_{45}H_{45}O_{10}Br_5$ (79 Br and 81 Br)), 1142.4, 1144.4, 1146.4 1148.4 ($[M+H]^+$, for $C_{45}H_{45}O_{10}Br_5$ (79 Br and 81 Br)), 1149.4 (M^+, calculated: 1149.4 for $C_{45}H_{45}O_{10}Br_5$ (81 Br)), 1150.4 ($[M+H]^+$, calculated: 1149.4 for $C_{45}H_{45}O_{10}Br_5$ (81 Br)).

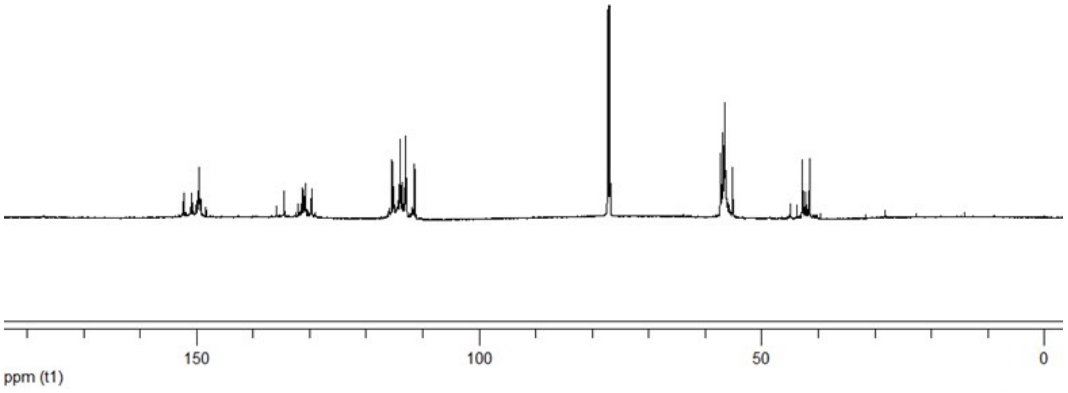


Figure S3. ^{13}C NMR (500 MHz, chloroform-d, 25 °C, TMS) spectrum of BDMP5.

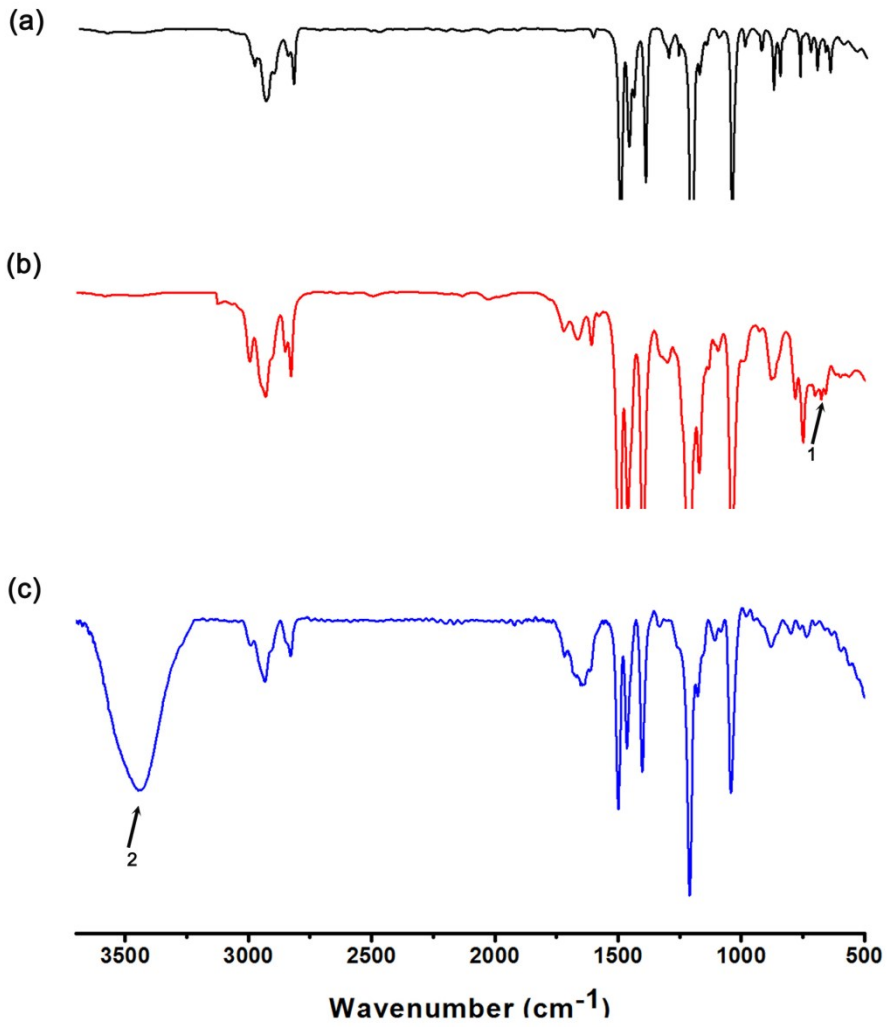


Figure S4. Fuorier transform IR spectrum of a) DMP5 (black line), b) BDMP5 (red line), c) purified polymer nanocapsules (blue line) (polymer nanocpsules come from the sample of BDMP5 reacted with hexanediamine (with mole ratio 1: 5.2)). From the FTIR spectra of BDMP5, as compared to those of DMP5, the peak of 676 cm^{-1} (arrow 1) corresponding to C-Br stretching vibrations occured. On the other hand, compared to BDMP5, the FTIR spectrum of nanocapsules shows that the wavenumber of 676 cm^{-1} corresponding to C-Br stretching dispeared and the peak of 3300-3500 cm^{-1} corresponding to N-H stretching occur (arrow 2).

Synthesis of disulfide polymer nanocapsule

Cystamine dihydrochloride (21mg) and BDMP5 (30 mg) were dissolved into 30 mL MeCN. Then the reaction wasadded into 2 mL Triethylamine and stirred at 70 ^{o}C for 5 h in nitrogen atmosphere. After cooling to room temperature, the solution was dialyzed against water for 24 h to remove the MeCN and other unreacted agents.

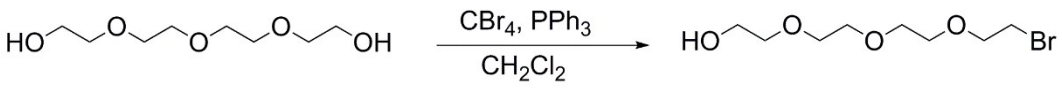
Preparation of 1,4-diaminobutane linked polymer nanocapsules

Butanediamine (8 mg) and BDMP5 (20 mg) were dissolved into 15mL MeCN. Then the reaction was stirred at 70 °C for 5 h in nitrogen atmosphere. After cooling to room temperature, the solution was dialyzed against water for 24 h to remove the MeCN and other unreacted agents.

Preparation of hexanediamine linked polymer nanocapsules in methanol

Hexanediamine (15.7 mg) and BDMP5 (30 mg) were dissolved into 30 mL methanol. Then the reaction was stirred at 50 °C for 5 h in nitrogen atmosphere. After cooling to room temperature, the solution was dialyzed against water for 24 h to remove the MeCN and other unreacted agents.

Synthesis of 2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethan-1-ol



Scheme S2. Synthesis rout of 2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)- ethan-1-ol.

The synthesis of 2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethan-1-ol was carried out similarly to previous work[3] and the synthesis rout was shown in scheme S2. To a solution of tetra (ethylene glycol) (5.26 g, 27.1 mmol) in dichloromethane (50 mL) at 0°C was added carbon tetrabromide (3.00 g, 9.05 mmol) and triphenylphosphine (2.61 g, 9.95 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 2hours, and the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography (hexane/ethylacetate=1/2) to afford 1.50 g (64%) product as yellowish oil. ^{1}H-NMR (500 MHz, $CDCl_3$, 25℃, TMS) (figure S5): δ (ppm): 3.48 (t, 2H), 3.61 (t, 2H), 3.68 (s, 8H), 3.73 (t, 2H), 3.81 (t, 2H). ESI-TOF mass spectrum (Figure S6): m/z 257.3 ($[M+H]^+$, calculated: 256.03 for $C_8H_{17}O_4Br$ (79Br)); 259.3 ($[M+H]^+$, calculated: 258.03 for $C_8H_{17}O_4Br$ (81Br))

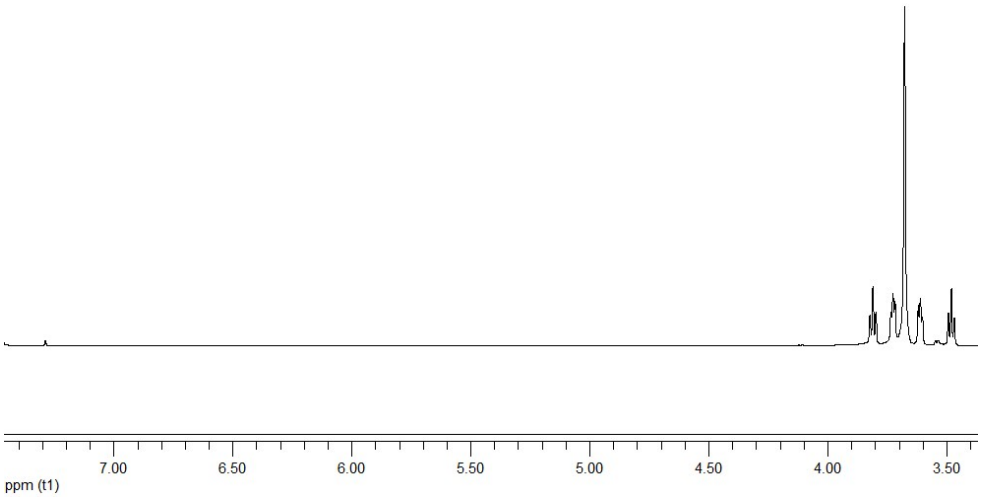


Figure S5. ^{1}H-NMR (500MHz, $CDCl_3$, 25℃, TMS) spectrum of 2-(2-(2-(2-bromoethoxy)ethoxy)-ethoxy) ethan-1-ol.

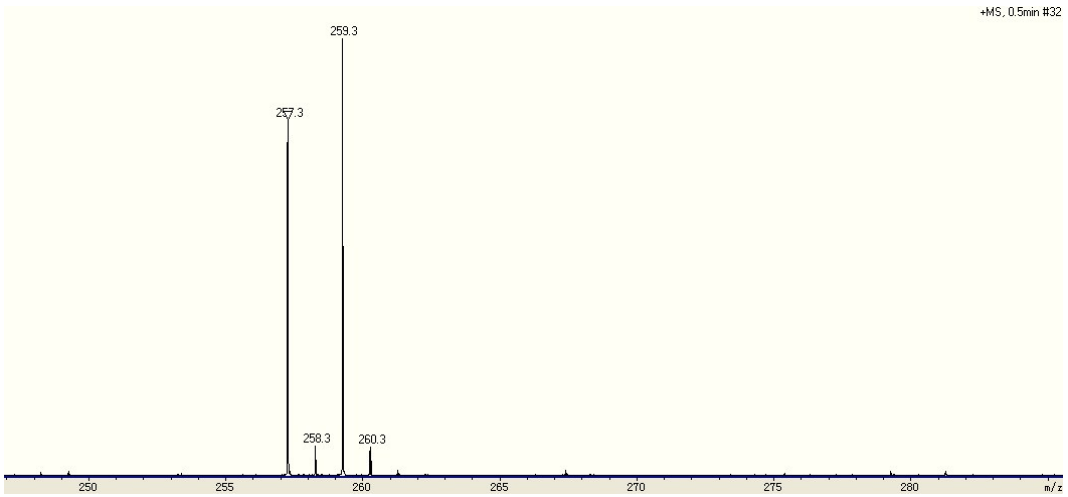


Figure S6. ESI-TOF mass spectrum of compound.

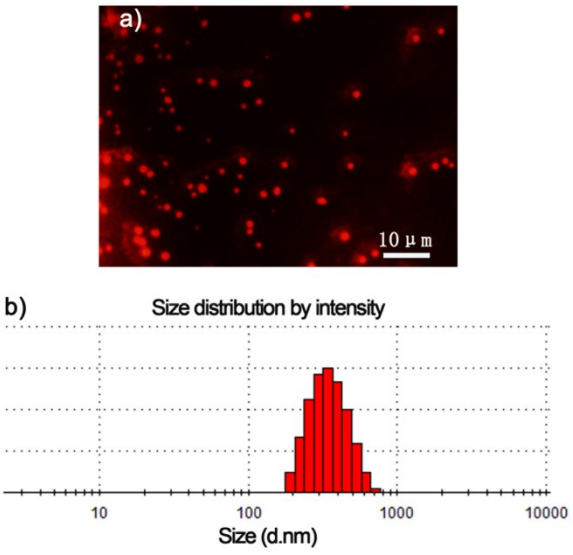


Figure S7. a) Fluoroscopic image (rhodamine B (RHB) as the fluorescent dye); b) DLS data (size distribution by number). The polymer nanocapsules came from system that BDMP5 (30mg) reacted with hexanediamine (15.7mg) in acetonitrile (MeCN) (30mL).

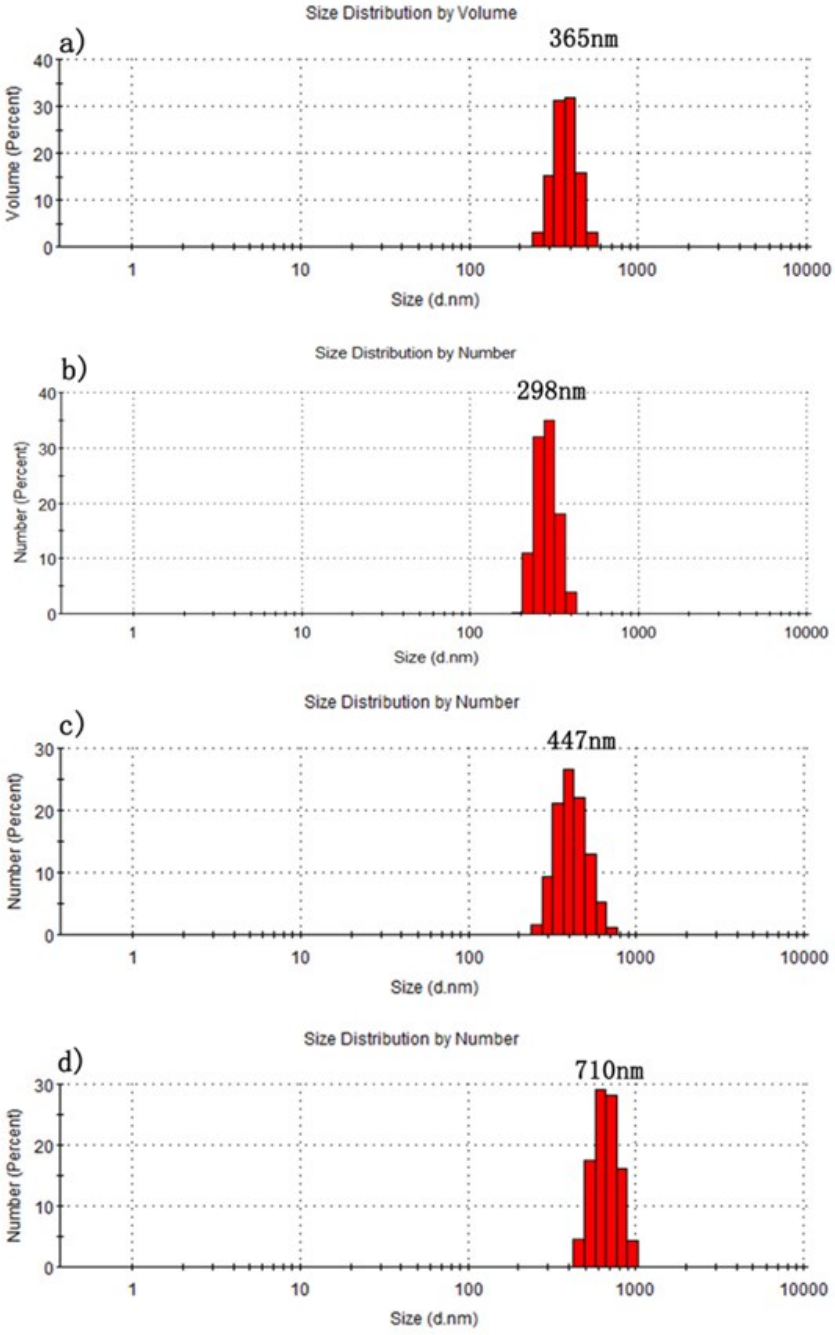


Figure S8. Dynamic light scattering studies of the polymerization of BDMP5 with different length of linkers (distribution by number). a) Polymerization of BDMP5 reaction with cystamine dihydrochloride ($NH_2CH_2CH_2S$-$SCH_2CH_2NH_2$) (about as same length as hexanediamine). b) Polymerization of BDMP5 reaction with butanediamine in MeCN. c) Polymerization of BDMP5 reaction with hexanediamine in MeOH. d) Polymerization of BDMP5 and hexanediamine in MeOH (excess mole ratio).

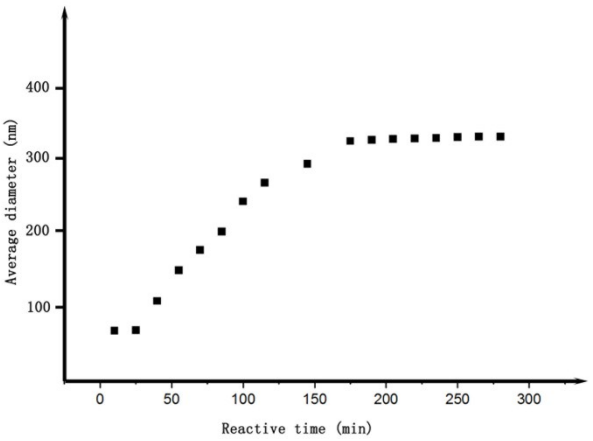


Figure S9. The change of the average size (observed by DLS) during the formation of polymer nanocapsule by covalent self-assmebly of BDMP5 and hexanediamine.

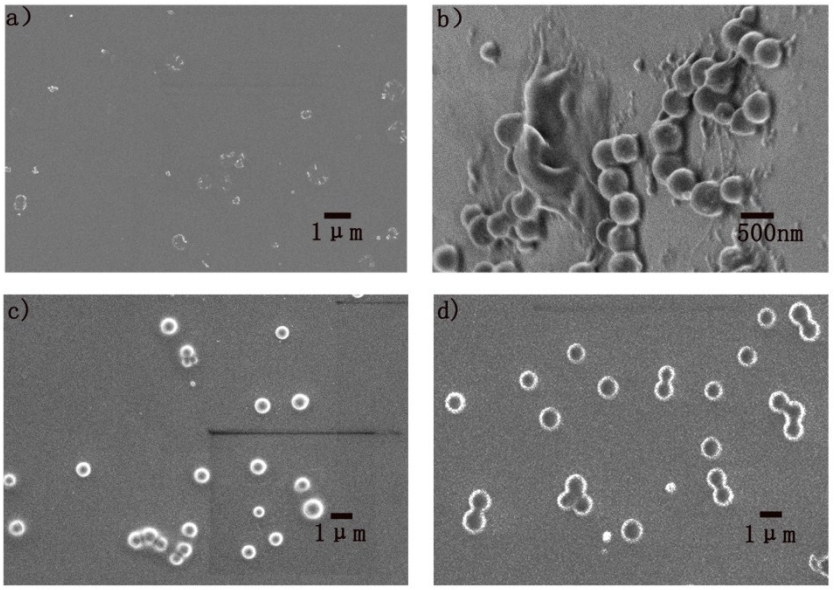


Figure S10. SEM images of covalent self-assembly process from covalent self-assembly of BDMP5 (30.0 mg) and hexanediamine (15.7 mg) in MeCN (30 mL) in the presence of N_2 at 70 ℃). A), B), C), D) were the same sample at different time. A) Before heating. B) After 1.5 h. C) After 2.5h. D) Final morphology.

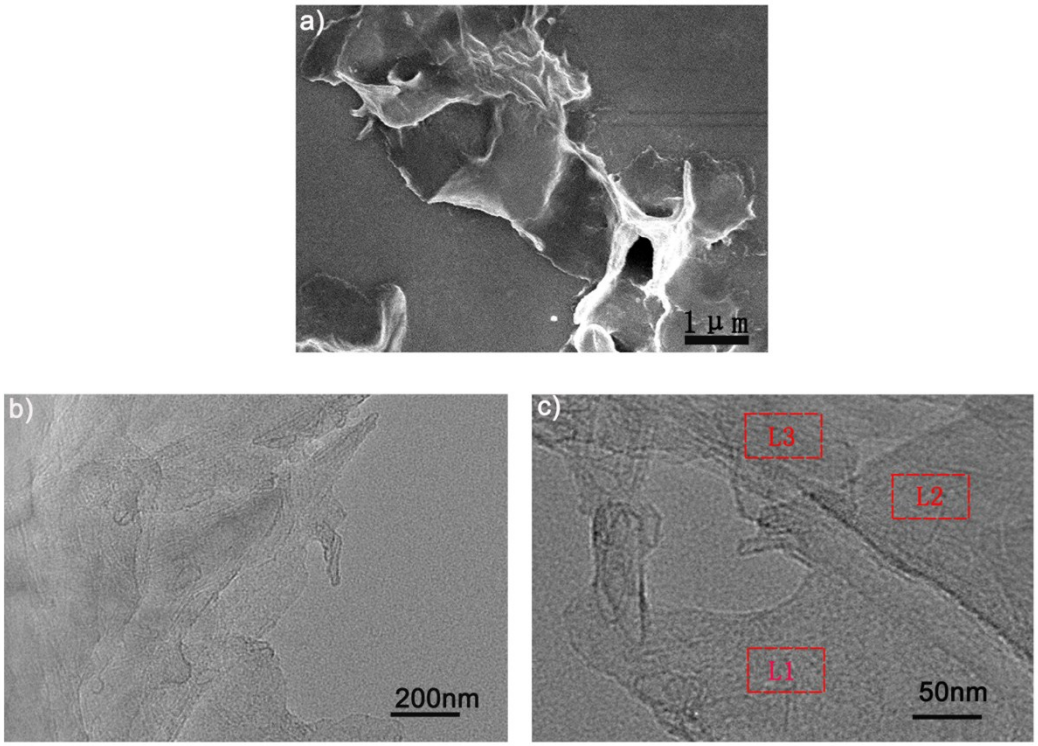
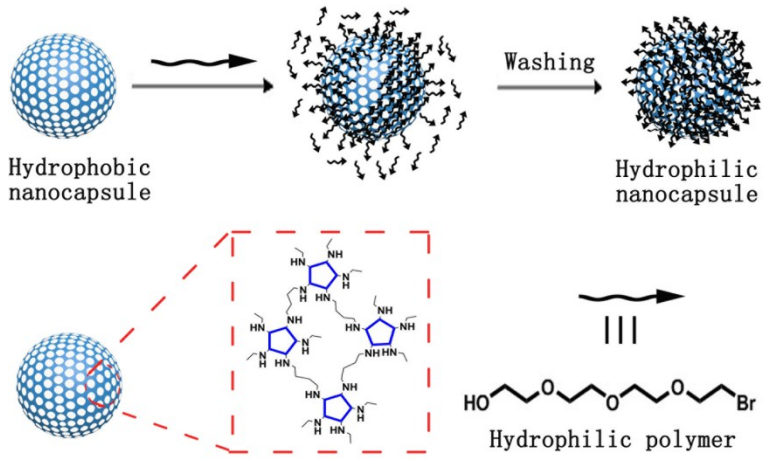


Figure S11. a) SEM image of the microscale polymer films; b) and c) TEM images of the multilayer polymer films. The red arrows showed the multilayered polymer films (the arrow1 pointed to the bottom film and the arrow 2 pointed to the interlayer film and the arrow 3 pointed to the top layer film).



Scheme S3. Scheme of preparing hydrophilic polymer nanocapsules.

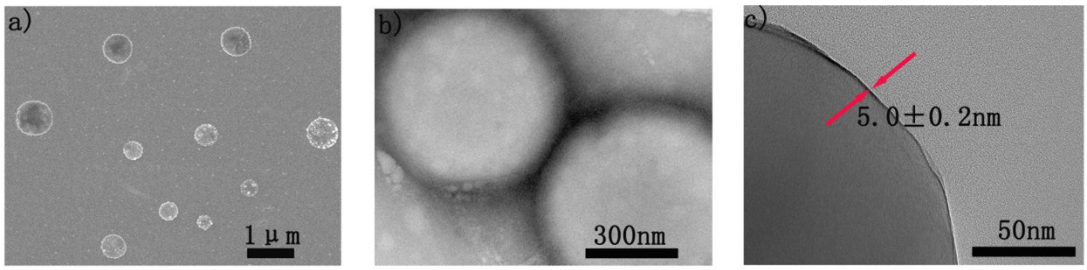


Figure S12. a) SEM image of hydrophilic nanocapsules. b) and c) TEM images of hydrophilic nanocapsules. The thickness of them was about 5nm. 4) Fluoroscopic image (rhodamine B (RHB) as the fluorescent dye).

References:

1. (a) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, 130, 5022-5023. (b) Ogoshi, T.; Kitajima, K.; Yamagishi, T.-a.; Nakamoto, Y. *Org. Lett.* **2010**, 12, 636–638. (c) Ogoshi, T.; Kitaji**ma**, K.; Aoki, T.; Fujinami, S.; Yamagishi, T.-a.; Nakamoto, Y. *J Org. Chem*. **2010**, 75, 3268–3273.

2. (a) Kumar, S.; Chawla, H. M.; Varadarajan, R. *Tetrahedron Letters,* **2002**, 43, 7073–7075. (b) Klenke, B.; Näther, C.; Friedrichsen, W. *Tetrahedron Letters,* **1998**, 39, 8967-8968.

3. (a) Lee, J.; Jeong, E. J.; Kim, J. *Chem. Commun.* **2011**, 47, 358-360. (b) Cao, P.-F.; Mangadlao, J.; Advincula, R. *Angew. Chem., Int. Ed.,* **2015**, 127, 5216–5220.