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Cucurbit[8]uril-Based Water-Soluble Supramolecular Dendronized Polymer: Evidence from Single Polymer Chain Morphology and Force Spectroscopy

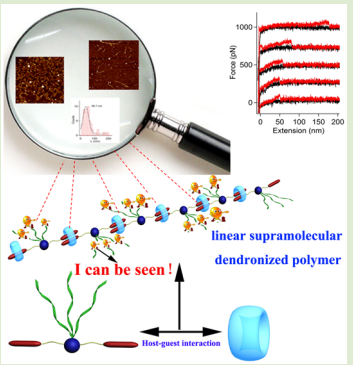
Jia-Fu Yin,[†,‡] Yi Hu,[§] De-Gao Wang,[†] Lan Yang,[†,‡] Zhong Jin,*[,§] Yi Zhang,*[,‡] and Gui-Chao Kuang*[,†]

[†]State Key Laboratory of Power Metallurgy, Department of Polymer Materials and Engineering, and [‡]College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

[§]Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

Supporting Information

ABSTRACT: A novel water-soluble supramolecular dendronized polymer (SDP) was prepared through cucurbit[8]uril (CB[8])-naphthalene host–guest interaction. The composition ratio between BDP and CB[8] of as-prepared luminescent supramolecular polymer was confirmed by ^{1}H NMR technique and mass spectrometry. In addition, atomic force microscopy (AFM) images showing the polymer chain length up to 150 nm and height up to 1.75 nm unambiguously demonstrate the supramolecular polymer formation. This work might be useful for designing other main chain supramolecular dendronized polymers.



Supramolecular dendritic polymers have gained considerable attention in the last two decades due to their dynamic and reversible capabilities.[1−3] Various kinds of supramolecular dendritic polymers showing responses to external stimulus have been developed for functional materials.[4−8] Among them, supramolecular dendronized polymers (SDPs) have exhibited special characteristics for versatile topological structures.[9] This type of polymers have been realized through "graft-to" method to obtain side chain SDPs and macromonomer polymerization route to afford main chain SDPs.[10] Multiple hydrogen bonding, metal coordination, and $\pi-\pi$ interaction have been identified as driving forces to prepare main chain SDPs, respectively.[11−17] Nevertheless, there is still rare report referring to the architecture of main chain SDP through formation of host–guest complex, although this strategy has been well-developed in preparation of side chain SDPs.[18−20]

On the other hand, cucurbit[8]uril (CB[8]) based supramolecular polymers have been widely investigated because CB[8] is a versatile host to stabilize the supramolecular polymers.[21−25] The guest molecules could be encapsulated by CB[8] with high binding constants include neutral structures such as naphthyl, coumarin, azobenzene, tryptophan or anthryl groups and positive charge moiety such as viologen, thiazole orange, or cyanostilbene derivatives.[26−34] Despite great progresses in this field, CB[8] based high degree supramolecular polymers in aqueous solution are still not easy to be obtained due to the poor solubility of CB[8] and conjugated monomer molecules. Moreover, to avoid intermolecular cyclization at low concentration is an important concern. In this regard, Zhang and co-workers developed a series of CB[8] based supramolecular polymers in water by rational designed monomers.[35] We are particularly interested in utilizing water-soluble dendritic monomers to prepare CB[8] based main chain SDP, as it not only could resolve the cyclization problem, but also the polymer could be visualized by AFM images intuitively due to the bulky side dendritic groups.

Boron-dipyrromethene (BODIPY) dyes and its derivatives have been widely investigated for their versatile functions in many fields. Wang and co-workers have successfully fabricated a kind of supramolecular vesicles through the host–guest interaction between BODIPY derivatives and pillar[5]arene.[36] In this contribution, we produced BODIPY derivative BDP as a building block to construct CB[8] based main chain SDP. Two naphthyl units were attached to the 2,6-position of the dye to provide the binding sites while the dendritic oligo(ethylene glycol) (OEG) was modified at the meso position to increase the water solubility. The positively charged pyridinium moiety of BDP was introduced to increase the binding affinity between CB[8] and BDP, since the carbonyl groups of the CB[8] portals favor cationic moieties due to ion-dipole effect. The naphthyl units would be accommodated in the cavity of CB[8] to form a dimer, and then the

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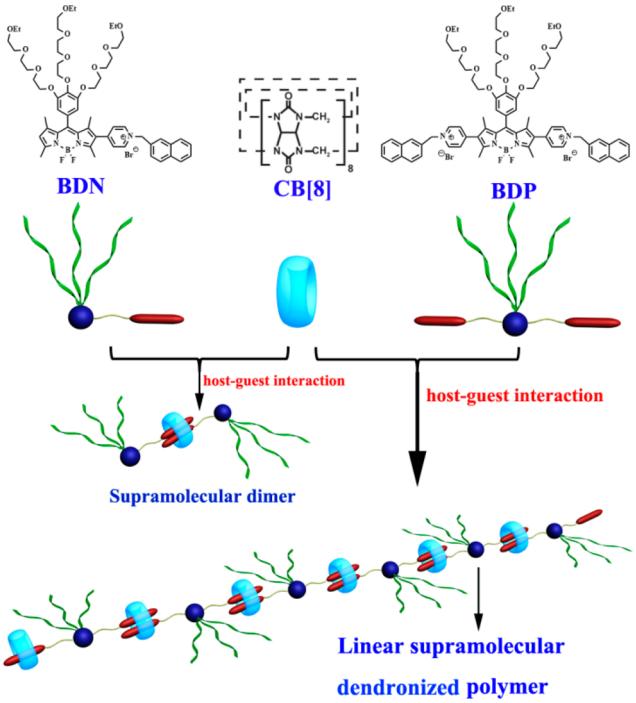
supramolecular polymer would be achieved by the host enhanced $\pi-\pi$ interaction. Mononaphthyl substituted BODIPY derivative BDN was prepared as a model molecule for comparison (Scheme 1).

Scheme 1. Cartoon Representation of Host-Guest Interaction between BDN and CB[8] and between BDP and CB[8]



The synthesis of monomer was started from OEG modified BODIPY, which was reported in our previous literature.[37] After iodination by iodine and iodic acid at the 2,6-position of BODIPY, the iodinated product underwent Suzuki coupling reaction with 3-pyridineboronic acid to give rise the bispyridine substituted compounds. The final product BDP with two naphthyl units would be obtained by addition excess of 2-(bromomethyl) naphthalene. Model compound BDN was synthesized by similar procedure except the first step by using N-bromosuccinimide (NBS) for bromination. The synthetic details were described in Supporting Information.

The CB[8] based SDP was characterized by a combination of NMR techniques. ^{1}H NMR titration experiments were performed to verify the binding ratio of the BDP and CB[8] (Figure 1). The monomer BDP peaks were well-resolved when no CB[8] was added. After the molar ratio increased to 1:0.25, the peaks at 4.21, 5.62, and 5.86 ppm ascribed to CB[8] could be observed (Figure 1f), accompanying by the unexpected disappearance of signals of naphthyl group. This result indicated the naphthyl groups have been successfully encapsulated by the CB[8] molecules. As the CB[8] further addition, the intensities of CB[8] peaks increased gradually and the other peaks changed slightly. When the molar ratio reached 1:1, the spectrum showed no change, indicating the binding ratio is 1, which was consistent with previous reports that one CB[8] could encapsulate two naphthyl groups.[35] Moreover, the resolution of the peaks decreased upon the addition of CB[8] was also observed, suggesting the formation of supramolecular polymer. In order to further verify the binding stoichiometry,

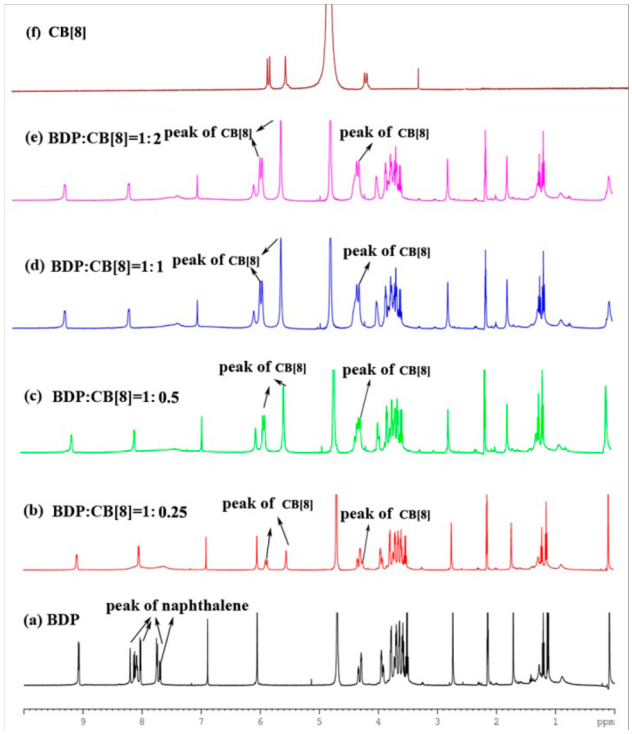


Figure 1. ^{1}H NMR spectra of BDP monomer with different molar ratio of CB[8] addition in D_2O.

high resolution mass spectrometry was introduced. The corresponding peak of 2:1 host−guest complex of BDN and CB[8] (2BDN + CB[8]) that located at m/z = 1735.1708, which referred to the (2BDN + CB[8]-2Br-)/2 was detected[30] (Figure S1). The above two points was sufficient to reveal the binding ratio of 1:1 between BDP and CB[8].

As a widely used technique to characterize supramolecular polymer, 2D ^{1}H NMR nuclear Overhauser effect spectroscopy (NOESY) experiments were performed to further elaborate the binding behaviors between our targeting molecules and CB[8] (Figure 2). The 2:1 mixture of BDN and CB[8] in D_2O was studied first (Figure S2). The correlations between the proton of CB[8] and the H_b, H_c, and H_d from BDN through the space were detected, confirming that the supramolecular dimer formed. The 2D ^{1}H NMR of a 1:1 mixture of BDP and CB[8] gave more evidence for the CB[8] host naphthyl $\pi-\pi$ interaction. A strong correlation spot could be observed between the naphthyl group and CB[8]. In addition, the protons H_d form the methylene linked to the pyridine and the protons H_b and H_c from pyridine show similar correlations with CB[8] as 2:1 mixture of BDN and CB[8].

The formation of SDP was evidenced by 2D ^{1}H NMR diffusion-ordered NMR spectroscopy (DOSY). For free BDP solution in D_2O (4 mM), the D value was determined to be 1.41×10^{-10} m^2s^{-1}. When the same concentration of BDP was added one equivalent of CB[8], the D value of the mixture solution decreased to be 7.24×10^{-11} m^2s^{-1}, suggesting the formation of SDP (Figure 3). Furthermore, dynamic light scattering experiments (DLS) were introduced to provide more evidence of the construction of SDP. The SDP size would increase with the mixture concentration, indicating that high concentration facilitated to form high polymerization degree SDP (Figure S3). In addition, the photophysical properties of the SDP demonstrated that the fluorescence intensities were

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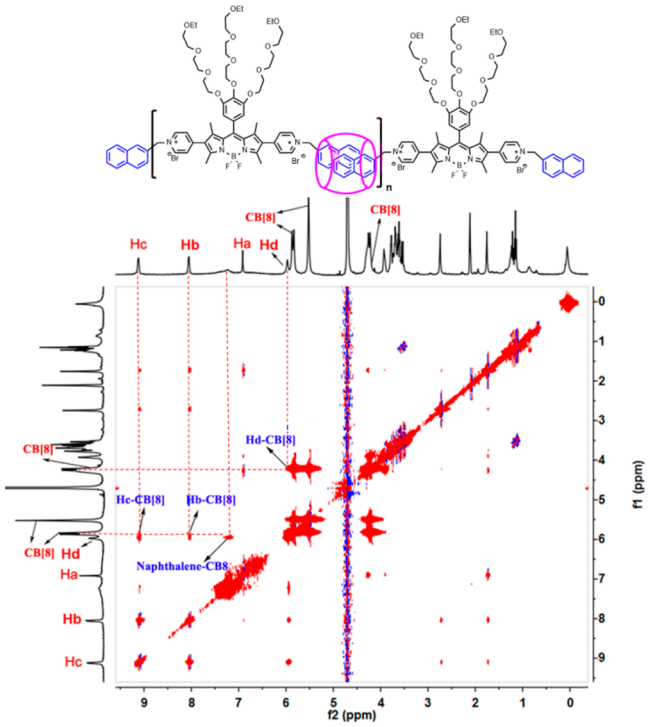

Figure 2. 2D ^{1}H NMR NOESY spectrum of a mixture of BDP and CB[8] (1:1, 2 mM) in D_2O.

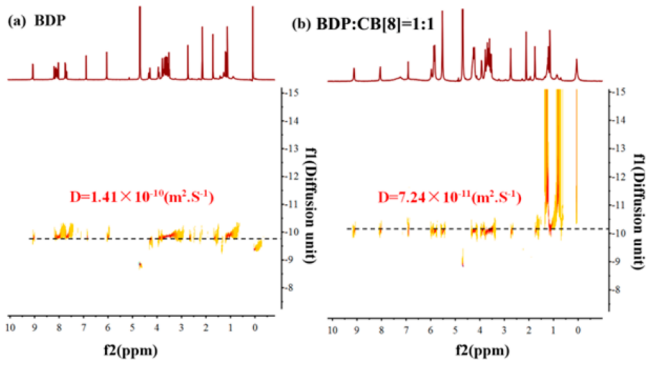

Figure 3. DOSY-NMR spectrum (500 MHz) of the solution of (a) BDP (4 mM) and (b) mixture of BDP and CB[8] (1:1, 4 mM) in D_2O.

dependent on the polymerization degree. The fluorescence would show enhancement during the polymerization upon the CB[8] addition (Figure S4). But the fluorescence intensities would decrease when the SDP depolymerized upon heating (Figure S5).

Atomic force microscopy (AFM) was conducted to visualize the single main chain SDP morphology. Due to the bulky side group, the single polymer chain with extended conformation could be expected; although rare report referred to the host stabilizes SDP has been demonstrated. The AFM sample was prepared by spinning the dilute aqueous supramolecular solution (0.005 mM) at high speed (5000 r/m) on mica. Only aggregates would be detected at higher concentration or slow speed (Figure 4a). Typical AFM images for this CB[8] host SDP were shown at Figure 4b,c. Single supramolecular polymer chains are clearly identified with different magnification. The length of some polymer chain was determined to be as long as more than 150 nm, which indicated that high degree

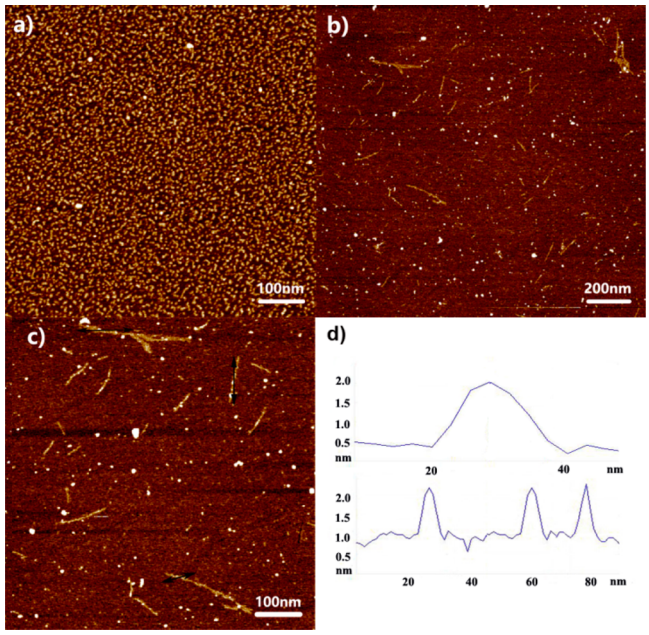

Figure 4. AFM images of main chain SDP prepared from different aqueous concentration of BDP and CB[8] (1:1) (a) 0.1 mM and (b, c) 0.005 mM. (d) Height image from (c).

polymers were obtained. Considering the flexible OEG side group are about 1.0 nm at vertical position,[38] we expected that the highest position of the polymer chain might come from CB[8], which shows its outer diameter 1.75 nm, this value was consistent with the determined height from AFM image (Figure 4d). Therefore, we believe that this main chain SDP should be necklace morphology.

AFM-based single-molecule force spectroscopy (SMFS) measurement was performed to further investigate molecular scale information.[39,40] Actually, the supramolecular polymer could be picked up at a random position by AFM tip. Therefore, the force−extension curve was determined by the short chain between the hydrophilic substrate and AFM tip. Representative curves of the supramolecular polymer at 0.04 mM were depicted in Figure 5a, which showed typical covalent polymer chain stretching curves. Statistical data was obtained by Gaussian fitting curve and the probable length of SDP was calculated to be 38.7 nm, which was comparable to the well-developed supramolecular polymers by Zhang.[30,35] Considering the true length should be much longer than this value because

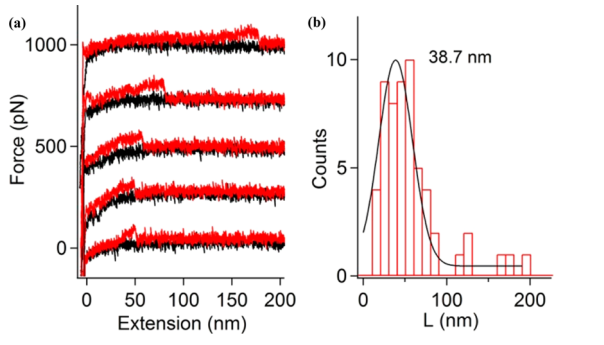

Figure 5. (a) Representative force−extension curves. (b) Histogram of the lengths of the force peaks; the Gaussian fitting length of the supramolecular polymer was calculated to be 38.7 nm.

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the site picked by AFM tip was random, we were sure that the supramolecular polymerization was highly efficient with a relative high degree.

In this letter, we developed a novel SDP through host−guest interaction between CB[8] and BDP. Various NMR techniques were performed to evidence this supramolecular polymer formation. This novel linear SDP was able to be visualized intuitively by AFM due to the existence of bulky side groups. AFM image unambiguously demonstrated the single main chain supramolecular polymer with exact height equal to the outer diameter of CB[8]. SMFS experiments further illustrated the formation of a linear supramolecular polymer. In summary, we have utilized a relatively new way to construct main chain SDP that could be observed. Considering the biocompatibility of CB[8] and BODIPY dyes, this work might be useful for photodynamic therapy, which shows promising application in biomedical materials. Further work on this aspect to design biomedical material based on BODIPY dyes and CB[*n*] is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00973.

Synthetic details of all compounds, UV−vis and fluorescence spectra, DLS spectra, mass spectrometry, and NMR spectra (PDF).

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhongjin@nju.edu.cn.
*E-mail: yzhangcsu@csu.edu.cn.
*E-mail: gckuang@csu.edu.cn.

ORCID

Zhong Jin: 0000-0001-8860-8579
Gui-Chao Kuang: 0000-0002-6682-8260

Author Contributions

All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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