

## Controlled Synthesis of Supramolecular Concentric Toroid

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Supramolecular polymers have found a variety of application in materials science, nanotechnology, and biotechnology<sup>1</sup>. Control of shapes and sizes of supramolecular polymers is therefore of great importance<sup>2</sup>; although it remains a significant challenge.

Previously, we have reported pathway complexity in supramolecular polymerization of porphyrin derivative **6** (Fig. a). **6** has the capacity to form nanofiber and nanosheet structures, and we achieved the selective formation of one of these structures by mechanical stimuli<sup>3</sup>. Based on the mechanistic insight into this unique molecular assembly, we designed porphyrin **6FFZn** which has fluorinated side chains (Fig. a). Interestingly, **6FFZn** was found to self-assemble into concentric toroid (Fig. b). AFM observation unveiled the growth mechanism of concentric toroid (Fig. c-g). Based on this understanding, we succeeded in controlling the size of concentric toroid through seeded supramolecular polymerization (Fig. h)<sup>4</sup>.

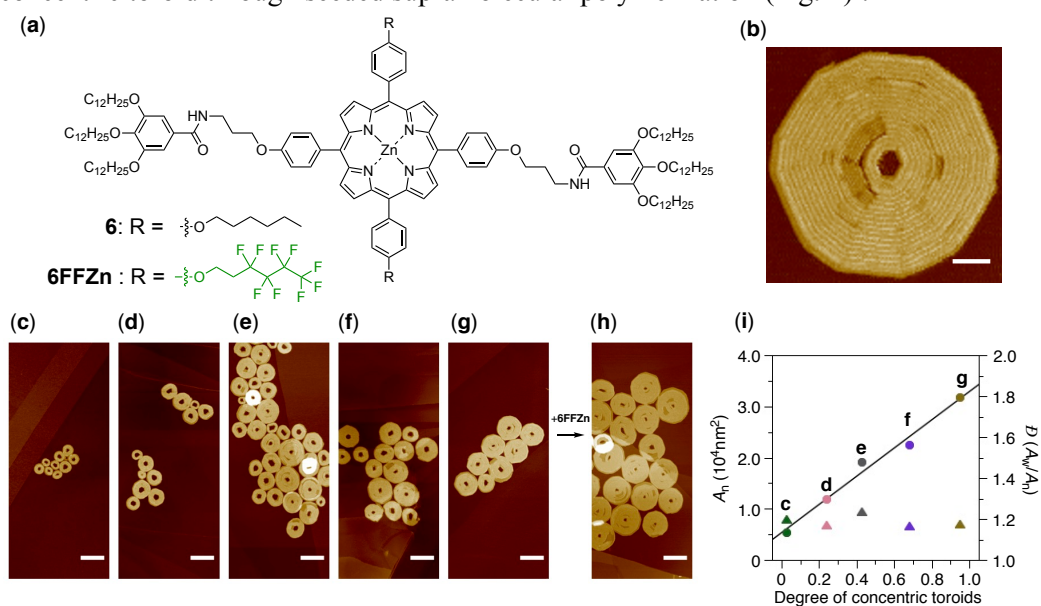


Figure (a) Structures of porphyrin derivatives (b) AFM image of concentric toroid of **6FFZn**. Scale bar, 50 nm. AFM images of concentric toroids obtained during the time-dependent evolution at (c) 60 s, (d) 180 s, (e) 300 s, (f) 480 s, (g) 1200 s, (h) 1800 s (i.e., after the incremental addition of a **6FFZn** solution). Scale bar, 200 nm. (i) Plot of number-average area ( $A_n$ ) and polydispersity ( $D$ ) of the concentric toroids as a function of the degree of the concentric toroids c-h.

- (1) T. Aida, E. W. Meijer, S. I. Stupp. *Science* **2012**, 335, 813-817. (2) A. K. Pearce, T. R. Wilks, M. C. Arno, R. K. O'Reilly. *Nat. Rev. Chem.* **2020**, 5, 21-45. (3) T. Fukui *et al.* *Nat. Chem.* **2017**, 9, 493-499. (4) N. Sasaki *et al.* *Nat. Commun.* **2020**, 11, 3578.