Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile preparation of one-dimensional nanostructures through polymerization-induced self-assembly mediated by host-guest interaction

Liangliang Shen, Yahui Li, Qunzan Lu, Xiaoliang Qi, Xuan Wu, and Jianliang Shen*

Abstract: Herein, a RAFT aqueous dispersion polymerization of ferrocenylmethyl acrylate (FCA) mediated by host-guest interaction between ferrocene meity and β-cyclodextrin was investigated. A series of peculiar one-dimensional morphologies can be readily obtained.

Experimental Procedures

Materials

Hydroxylmethylferrocene, poly (ethylene glycol) methyl ether ($mPEG_{113}$-OH, 5000 g/mol), acryloyl chloride, triethylamine, water-soluble initiator 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (AMD) and 2,3,6-tri-O-methyl-β-cyclodextrin (TM-β-CD) were purchased from J&K Scientific. Macromolecular chain transfer agent (CTA) PEG_{113}-CTA was synthesized according to a previously published procedure.[1]

Characterization

The chemical structure and monomer conversions of FCA and were confirmed by ^{1}H NMR analysis on a Bruker AV 400 MHz spectrometer. Gel permeation chromatography (GPC) measurement were performed on a Waters Alliance e2695 GPC system equipped with a Styragel guard column (WAT054415, 30 × 4.6 mm), two Org separation columns consisting of D2500 (300 × 8 mm) and D5000 (300 × 8 mm). Detection was made with a 2414 refractive index detector (Waters Alliance), a Viscotek 302/305 UV detector (Malvern Instruments), and a Viscotek TDA 305-020 LALS/RALS detector (Malvern Instruments). N, N-dimethylformamide (DMF, HPLC grade, containing 1.75 mg/mL LiBr) was used as the eluent at a flow rate of 0.7 mL/min. The morphology of nano-objects was characterized by TEM on a Jeol 200CX microscope. SEM was also used to analyze the morphology of nano-objects on a SU8010 microscope. Generally, a small drop of a sample solution (0.05-0.1% dispersed in water) was carefully dropped onto a carbon-coated copper grid (for TEM) or a silicon wafer (for SEM) and dried overnight at 25 °C under vacuum.

Synthesis protocol of FCA monomer

Hydroxylmethylferrocene (2.16 g, 10 mmol) and anhydrous triethylamine (3 mL) was firstly dissolved in anhydrous DCM (50 mL) and cooled to 0 °C in the ice bath. Then a DCM solution containing acryloyl chloride (0.99 g, 11 mmol) was added dropwise, followed by being stirred for 12 h. After the completion of this reaction, the solvent was removed under a vacuum. The resulting red solid was purified by column chromatography (n-hexane: DCM = 1:1, v/v) to afford the desired product as a red powder (2.16 g, 8 mmol, 80% yield). ^{1}H NMR was shown in Figure S1 (400 MHz, $CDCl_3$, 298 K) δ(ppm) 6.41 (dd, J = 17.3, 1.3 Hz, 1H), 6.11 (dd, J = 17.3, 10.4 Hz, 1H), 5.81 (dd, J = 10.4, 1.3 Hz, 1H), 4.98 (s, 2H), 4.34-4.09 (m, 9H).

Synthesis protocol of aqueous dispersion polymerization of FCA@TM-β-CD mediated by PEG_{113}-CTA

Before polymerization, a certain amount of FCA and TM-β-CD (mol/mol=1:1.2) were added into a glass vial with water under ultrasonication until complete dissolution. Then a certain amount of PEG_{113}-CTA and AMD were added. After the solution was bubbled with N_2 for 30 minutes, the glass vial was placed into an oil bath at 70 °C with a stirring speed of 500 rpm. After polymerization under nitrogen, the glass vial was removed from the oil bath and the solution was quenched by being exposed to air.

Redox reaction of the PEG_{113}-$PFCA_x$ BCP self-assembies

A molar excess of $FeCl_3$ dissolved in water was added into the PEG_{113}-$PFCA_x$ BCP self-assembies dispersion (3 mg/mL). Then the mixture was stirred for 24 h at room temperature and dialyzed against water for 24 h at room temperature. In order to reduce the above oxidized PEG_{113}-$PFCA_x$ BCP self-assembies, a molar excess of $SnCl_2$ dissolved in water was added. Then the mixture was stirred for 24 h and dialyzed against the water for 24 h at room temperature.

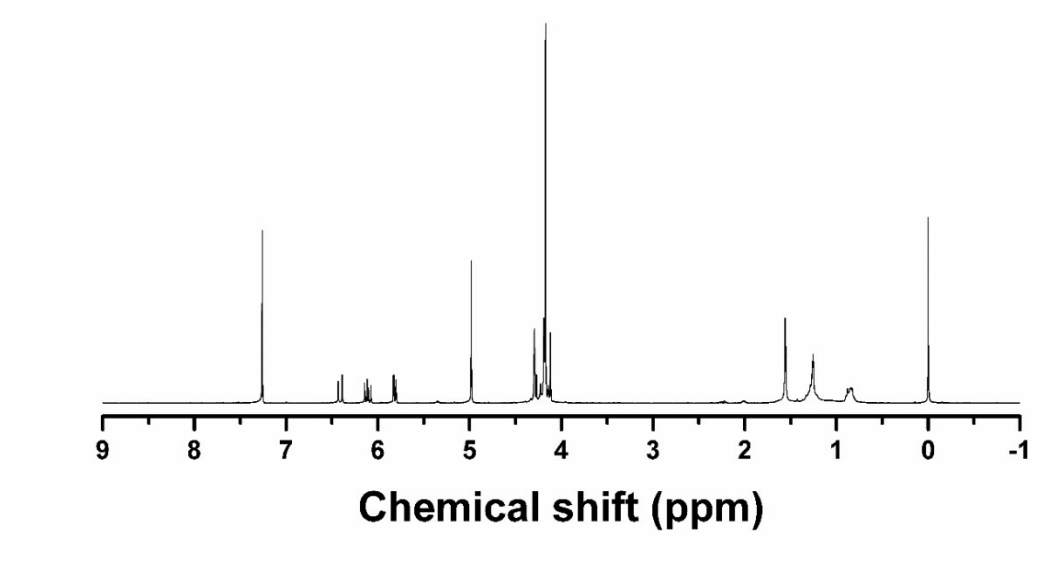

Figure S1. ^1H NMR spectrum of FCA in $CDCl_3$.

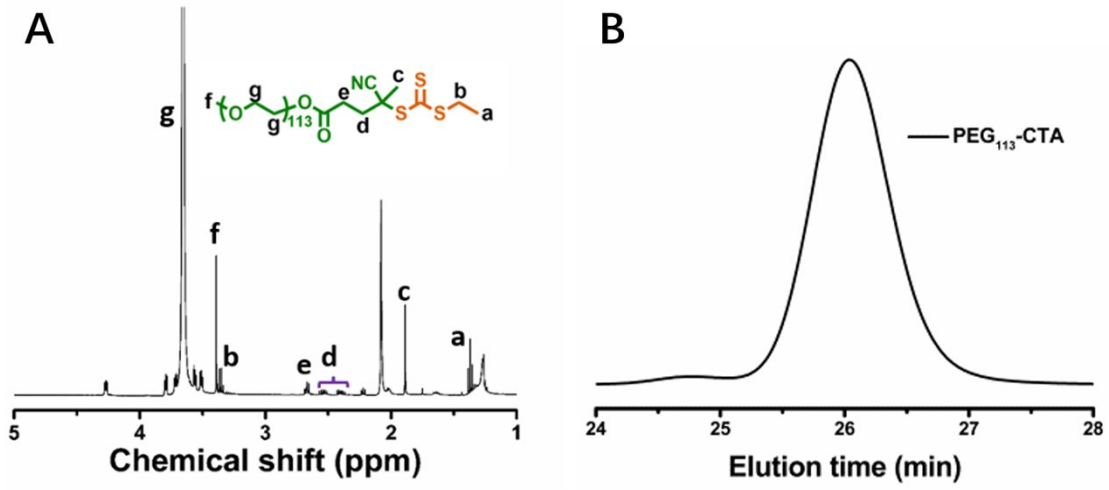

Figure S2. A) ^1H NMR spectrum of PEG_{113}-CTA in $CDCl_3$; B) GPC trace of PEG_{113}-CTA. Since the PEG_{113}-CTA used in this work and our previous work[2] is the same sample, the corresponding ^1H NMR spectrum and GPC trace are similar.

Table S1. Summary of the dispersion polymerization of TM-β-CD@FCA in water mediated by PEG_{113}-CTA at 70 °C, 4% w/v concentration of FCA.

PEG_{113}-CTA	FCA	TM-β-CD[a]	AMD[b]	Total Solids%[c]	Time (h)	*Conv.*% [d]

1	10	12	0.20	20	12	80
1	20	24	0.20	20	12	85
1	30	36	0.30	20	14	83
1	50	60	0.30	20	16	84
1	80	92	0.35	20	18	88
1	100	120	0.35	20	18	93

[a] In order to completely include FCA, the molar ratio of TM-β-CD to FCA was set as 1.2:1; [b] As for our PISA experiments with high DP of FCA, the amount of PEG_{113}-CTA we used was less than that used in PISA experiments with low DP of FCA. Therefore, in order to make sure that the polymerization went smoothly, we intentionally increased the molar ratio of initiator to PEG_{113}-CTA. [c] The total solids including PEG_{113}-CTA, FCA and TM-β-CD; [d] Monomer conversion determined by ^1H NMR spectroscopy in $CDCl_3$.

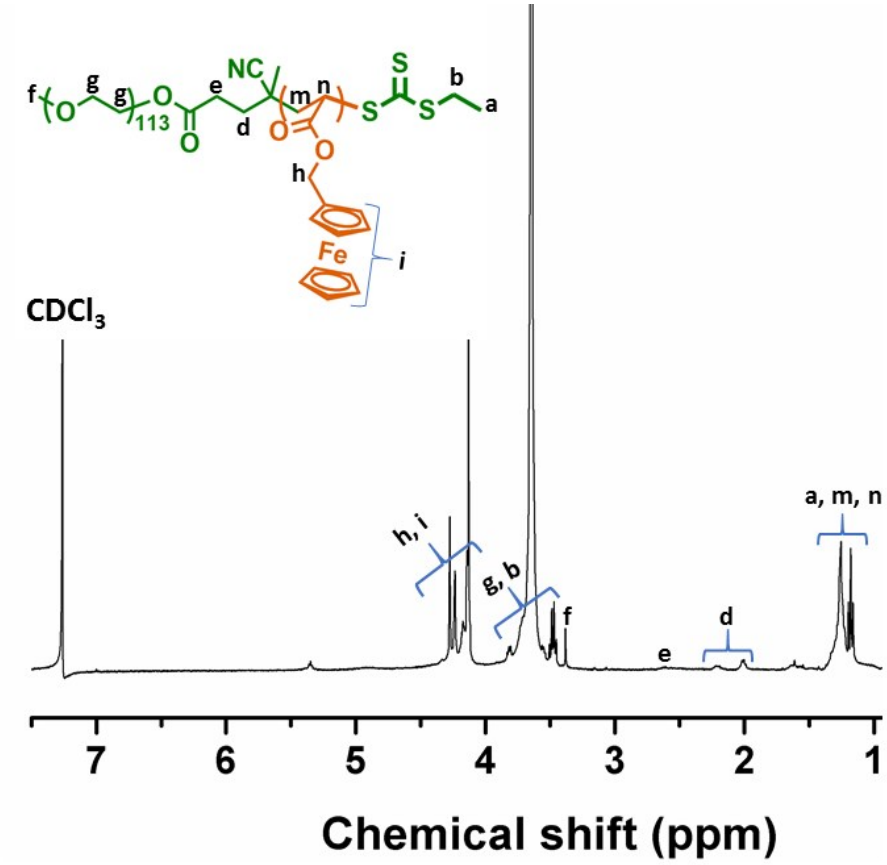

Figure S3. A) ^1H NMR spectrum of PEG_{113}-$PFCA_{42}$ block copolymer in $CDCl_3$ obtained in the aqueous PISA mediated by TM-β-CD at 70 °C, 4% w/v concentration of FCA.

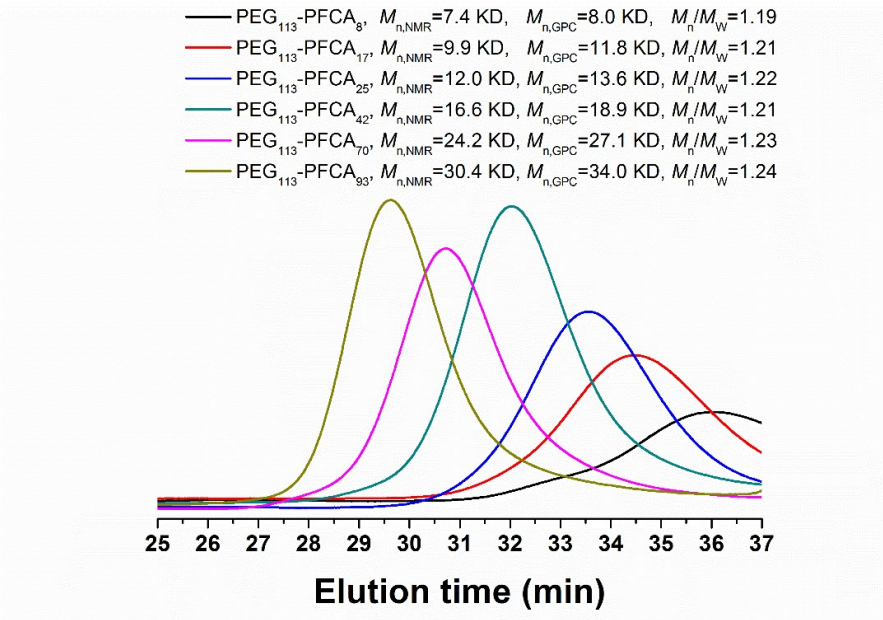

Figure S4. GPC traces of PEG_{113}-$PFCA_x$ block copolymers synthesized in the aqueous PISA mediated by TM-β-CD at 70 °C, 4% w/v concentration of FCA.

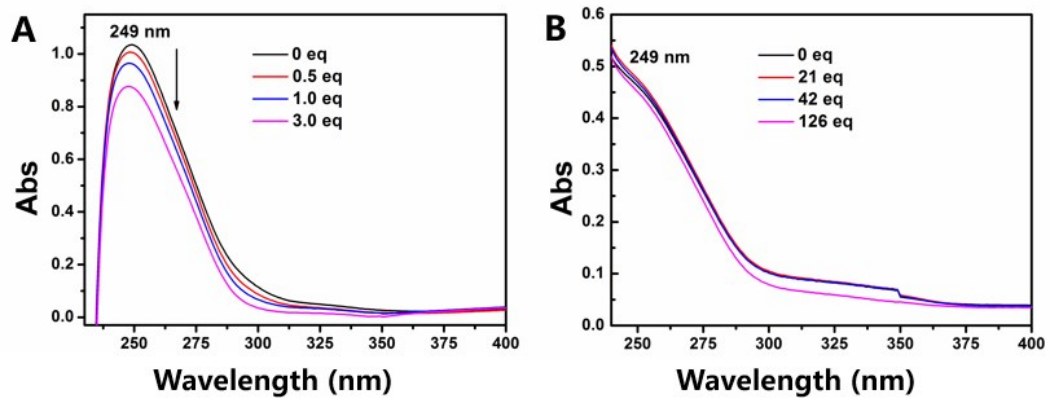

Figure S5. (A) UV-Vis spectra of FCA at a concentration of 2.0×10^{-4} M in aqueous solution upon the gradual addition of TM-β-CD from 0 to 3.0 eq.; (B) UV-Vis spectra of PEG_{113}-$PFCA_{42}$ at a concentration of 4.8×10^{-6} M in aqueous solution upon the gradual addition of TM-β-CD from 0 to 126 eq.

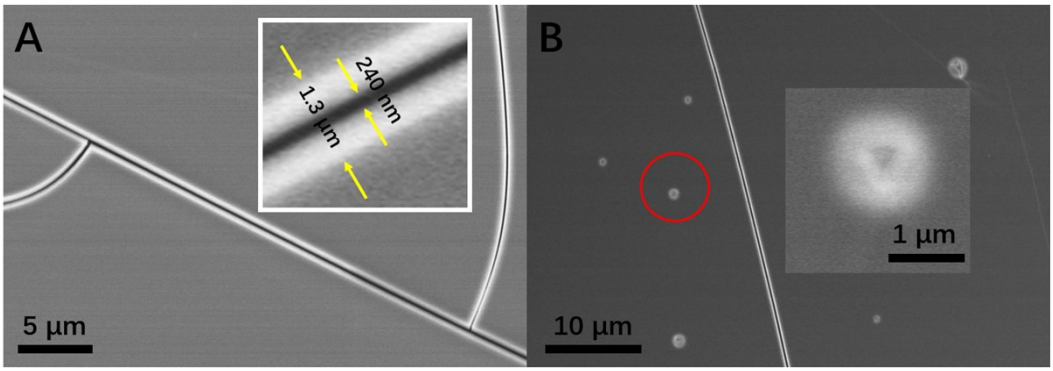

Figure S6. A, B) SEM images of PEG_{113}-$PFCA_{25}$ BCP nanotube in different locations, 4% w/v concentration of FCA;

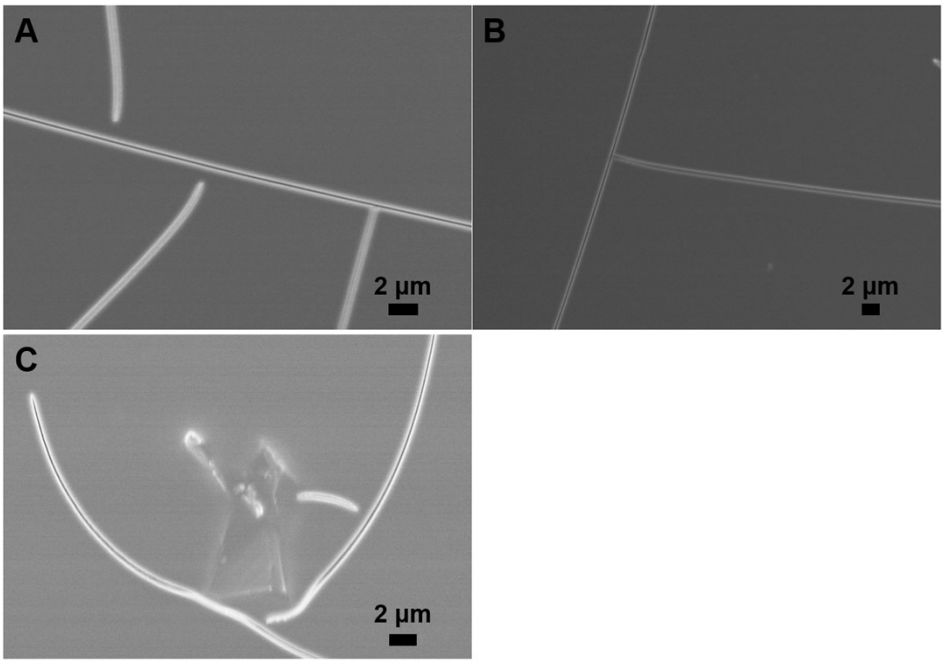

Figure S7. SEM micrographs of PEG_{113}-$PFCA_x$ self-assemblies in water mediated by TM-β-CD at 70 °C, 4% w/v concentration of FCA: A) PEG_{113}-$PFCA_{42}$; B) PEG_{113}-$PFCA_{70}$; C) PEG_{113}-$PFCA_{93}$.

Table S2. Summary of the dispersion polymerization of TM-β-CD@FCA in water mediated by PEG_{113}-CTA at 70 °C, 8% w/v concentration of FCA.

PEG_{113}-CTA	FCA	TM-β-CD[a]	AMD[b]	Total Solids%[c]	Time (h)	*Conv.*% [d]
1	20	24	0.15	35	12	90
1	30	36	0.15	35	12	93
1	50	60	0.20	35	14	94
1	80	92	0.25	35	18	93

[a] In order to completely include FCA, the molar ratio of TM-β-CD to FCA was set as 1.2:1; [b] As for our PISA experiments with high DP of FCA, the amount of PEG_{113}-CTA we used was less than that used in PISA experiments with low DP of FCA. Therefore, in order to make sure that the polymerization went smoothly, we intentionally increased the molar ratio of initiator to PEG_{113}-CTA. [c] The total solids including PEG_{113}-CTA, FCA and TM-β-CD ; [d] Monomer conversion determined by ^{1}H NMR spectroscopy in $CDCl_3$.

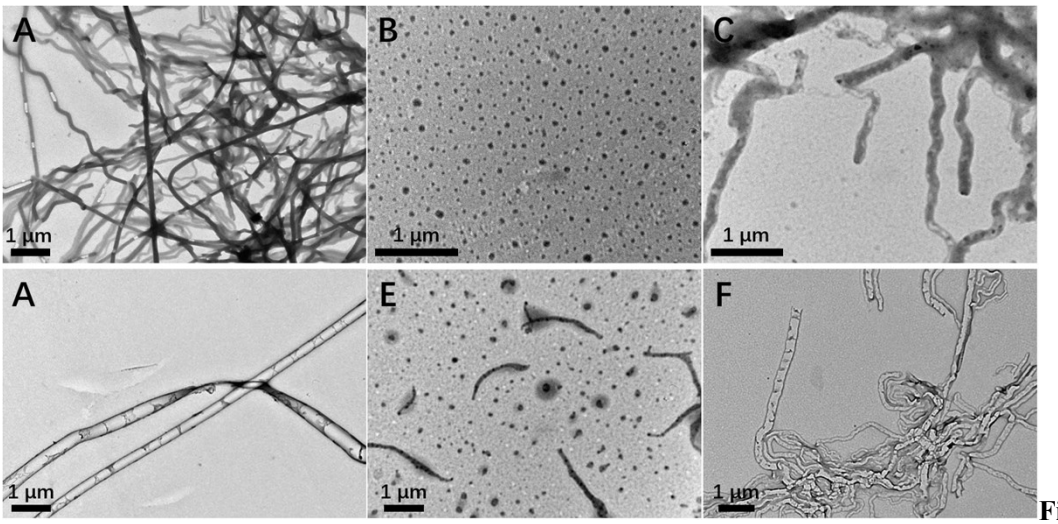

Figure S8. TEM micrographs of PEG_{113}-$PFCA_x$ BCP self-assemblies: A) PEG_{113}-$PFCA_{18}$ BCP nanowires, 8% w/v concentration of FCA; B) nanowires collapsed and finally dissociated into small spheres upon oxidation by $FeCl_3$; C) the intermediate transition morphology captured for nanowires; D) PEG_{113}-$PFCA_{70}$ BCP nanotubes, 4% w/v concentration of FCA; E) nanotubes collapsed and finally dissociated into small spheres upon oxidation; F) the intermediate transition morphology captured for PEG_{113}-$PFCA_{70}$ BCP nanotubes.

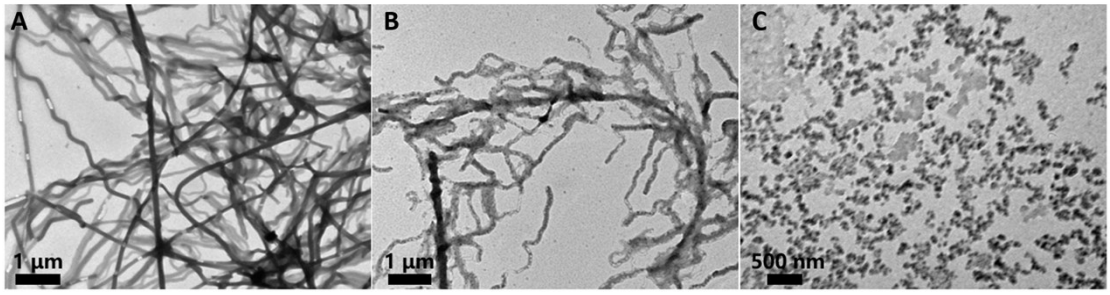

Figure S9. TEM micrographs of PEG_{113}-$PFCA_{18}$ self-assemblies, 8% w/v concentration of FCA: A) PEG_{113}-$PFCA_{18}$; B) PEG_{113}-$PFCA_{18}$ exposed to air for 30 days; C) PEG_{113}-$PFCA_{18}$ exposed to air for 60 days.

References

[1] W. Shen, Q. Qiu, Y. Wang, M. Miao, B. Li, T. Zhang, A. Cao, Z. An, *Macromol. Rapid Commun*. 2010, **31**, 1444-1448.
[2] L. Shen, H. Guo, J. Zheng, X. Wang, Y. Yang, Z. An, *ACS Macro Lett*. 2018, **7**, 287−292.