Electronic Supplementary Information

Homopolymer nanobowls with controlled size and denting degree

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1 Materials

Fuming nitric acid (95.0%), methanol (95.5%), N, N-dimethylformamide (DMF, 99.5%), ethanol (99.7%), hydrochloric acid (36.0~38.0%), CS_2 (98.0%), ethyl acetate (98.0%), diethyl ether (99.5%), and tetrahydrofuran (99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $NaBH_4$ (96.0%), 2,2'-bipyridine (99.0%) , CF_3COOH (99.5%), H_2O_2 solution (30.0%), NaOH (97.0%), dry Na_2SO_4 (99.0%), nitric acid concentrated solution (95.0%), Pd/C (10%), diatomite (19.6 μm), $MgSO_4$ (99.99%), acryloyl chloride (96.0%, 200 ppm MEHQ), triethylamine (99.0%), 2, 2'-azobis(2-methylpropionitrile) (AIBN), Na (99.7%), benzophenone (99.0%), KOH (99.9%), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (99.9%), phenylmagnesium bromide (1.0 M in THF), n-hexane (97.0%) and $CDCl_3$ (99.8%) were supplied by Aladdin Industrial. AIBN was recrystallized from methanol and stored at –25 °C. Concentrated sulfuric acid (93.0~98.0%) was offered by Alfa Aesar.

2 Characterization

2.1 Proton nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR spectra were recorded using a Bruker AV 400 MHz spectrometer at room temperature with $CDCl_3$ or DMSO-d_6 as solvents, and tetramethylsilane (TMS) as the standard. Samples (3 mg) were dissolved into 0.6 mL corresponding solvents for measurements.

2.2 Size exclusion chromatography (SEC)

Molecular weight (M_n) and polymer dispersity index ($Đ$) of polymers were measured by SEC. An Agilent 1260 Infinity SEC analysis system with two Shedex GPC KD series columns was used with HPLC grade DMF (containing 0.05 M LiBr) as eluent (flow rate of 0.8 mL min^{-1} at 50 °C). Samples (5 mg) were dissolved into 1 mL HPLC grade DMF and filtered before measurements.

2.3 Dynamic light scattering (DLS)

DLS measurements were performed on a Malvern ZS90 to analysis the hydrodynamic diameter (D_h), polydispersity (PD) and zeta potential (ζ) of nanoparticles in aqueous solution after dialysis. The scattering angle was fixed at 90°. Each sample was measured for three times, 6 runs per time, and 10 s per run. The temperature of measurement is in line with T_s.

2.4 Transmission electron microscopy (TEM)

TEM images were grabbed by JOEL JEM-2100F equipped with a Gatan 894 Ultrascan 1 k CCD camera or Hitachi H-800 at an accelerating voltage of 200 kV. To facilitate nanoparticles to disperse on copper grids, the surfaces of which were treated by plasma cleaner (HARRIK plasma, PDC-32 G) to make them more hydrophilic. 10 μL sample was dried on a grid at ambient temperature for at least 12 h.

2.5 Scanning electron microscopy (SEM)

SEM images were grabbed by FEI Quanta 200 FEG electron microscopy at 15 kV. The sample preparation procedure for SEM is the same as that for TEM with the addition of gold coating.

2.6 Fourier-transform infrared spectroscopy (FTIR)

The FT-IR spectra of homopolymers and the corresponding freeze-dried nanobowls self-assembled at 30 °C were obtained using a thermo Bruker EQUINOXSS/HYPERION2000 spectrometer. Each tablet used for testing was prepared by mixing 200 mg KBr and 1 mg sample powder.

2.7 Fluorescence spectroscopy

The fluorescence spectra were obtained via OLYMPUS, IX73 Fluorescence Microscope (New York Thermo Fisher Scientific). PBPy was dissolved into THF and freeze-dried nanobowls self-assembled at 20 °C were dissolved into deionized water at 0.1 mg mL^{-1}.

3 Experimental section

3.1 Synthesis of monomer *N*-([2,2'-bipyridyl]-4-yl)acrylamide

The monomer was synthesized in four steps (Fig. S1). The first three steps were achieved according to a previous protocol. [1] Afterward, 4-amino-2,2'-bipyridine (1.00 g, 5.85 mmol) and triethanolamine (TEA, 1.77 g, 17.5 mmol) were dissolved into anhydrous tetrahydrofuran (THF). Acryloyl chloride (0.794 g, 8.77 mmol) was diluted by anhydrous THF, and added into the former solution dropwise at 25 °C. The crude product was purified by column chromatography (n-hexane/EtOAc = 2/1 (v:v)).

3.2 Synthesis of 2-cyanopropan-2-yl benzodithioate (CPDB)

The THF solution of phenylmagnesium bromide (25 mL, 25 mmol) was added to the dried two-neck flask, and CS$_2$ (3.80 g, 50.0 mmol) was added dropwise. The reaction temperature and time were kept at 40 °C for 1 h. The solution was poured into ice water to remove the unreacted Grignard reagent. After adding concentrated hydrochloric acid (3.5 mL), the product was extracted from the aqueous phase by ether (50 mL × 3). Afterward, sodium thiobenzoate was extracted from the organic phase into the aqueous phase by NaOH solution (2.0 M, 25 mL × 3). Potassium ferricyanide aqueous solution (7.50 g in 75 mL) was added dropwise. After 30 min, the precipitate was filtered and dried. The product (3.06 g, 10.0 mmol) was dissolved in ethyl acetate (50 mL), and then AIBN (2.46 g, 15.0 mmol) was added. After refluxing for 18 h, the crude product was purified by column chromatography (n-hexane: ethyl acetate = 9:1 (v:v)).

3.3 Polymerization of poly(*N*-([2,2'-bipyridyl]-4-yl)acrylamide) (PBPy)

PBPy was synthesized via a RAFT process. The synthetic route is shown in Fig. S1. The monomer (299 mg, 1.33 mmol) was dissolved in *N*, *N*-dimethylformamide (DMF, 2.00 mL), then the chain transfer agent CPDB (294 mg, 0.133 mmol) and AIBN (1.00 mg, 6.09 × 10^{-3} mmol) were added into the solution. Degassed it for 30 min, and stirred it consecutively at 70 °C for 24 h under argon protection. After removing DMF by evaporation, the polymer was redissolved into dichloromethane and purified by precipitation in n-hexane three times. Then, it was dried in a vacuum oven to obtain PBPy as orange solid. ^{1}H NMR was carried out to determine the conversion of the monomer (Fig. S7). The molecular weight distribution (*Đ*) is 1.11 (Fig. S8). The ^{1}H NMR spectra of the monomer, intermediates, and CPDB are illustrated in Fig. S2-S6.

3.4 Self-assembly of PBPy

PBPy was dissolved in THF with a series of initial concentrations (C_{ini}) of 0.05, 0.1, 0.2, 0.3 mg·mL^{-1}. Deionized water as much volume as THF was dropwise added for four times, under slightly stirred at 200 r/min and 20 °C. The C_{ini} of 0.2 mg·mL^{-1} was applied to next experiments for relatively uniform nanobowls. To control the diameter and denting degree of nanobowls, on the one hand, deionized water was replaced by aqueous solution with a sequence of pH values, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, regulated by hydrochloric acid or NaOH, or with a set of Fe^{2+} concentrations adjusted by $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O_2$ on the other hand, the T_s was varied from 15 to 50 °C. THF was removed via dialysis against deionized water for 2 days. pH was measured by HANA HI98100 pH electrode probe.

4 Figures and tables
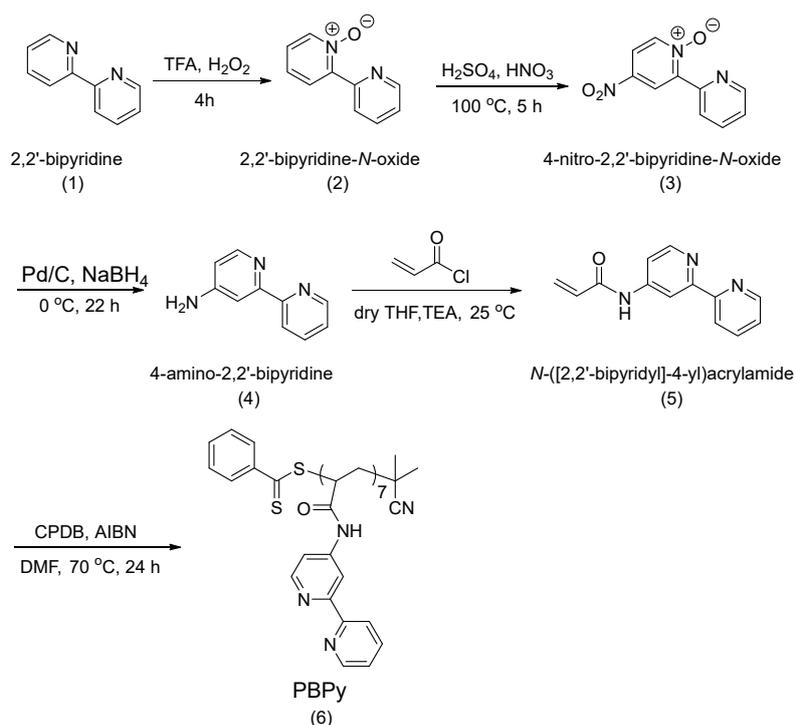
Fig. S1 Synthetic route to poly(*N*-([2,2'-bipyridyl]-4-yl)acrylamide) (PBPy) by RAFT polymerization.
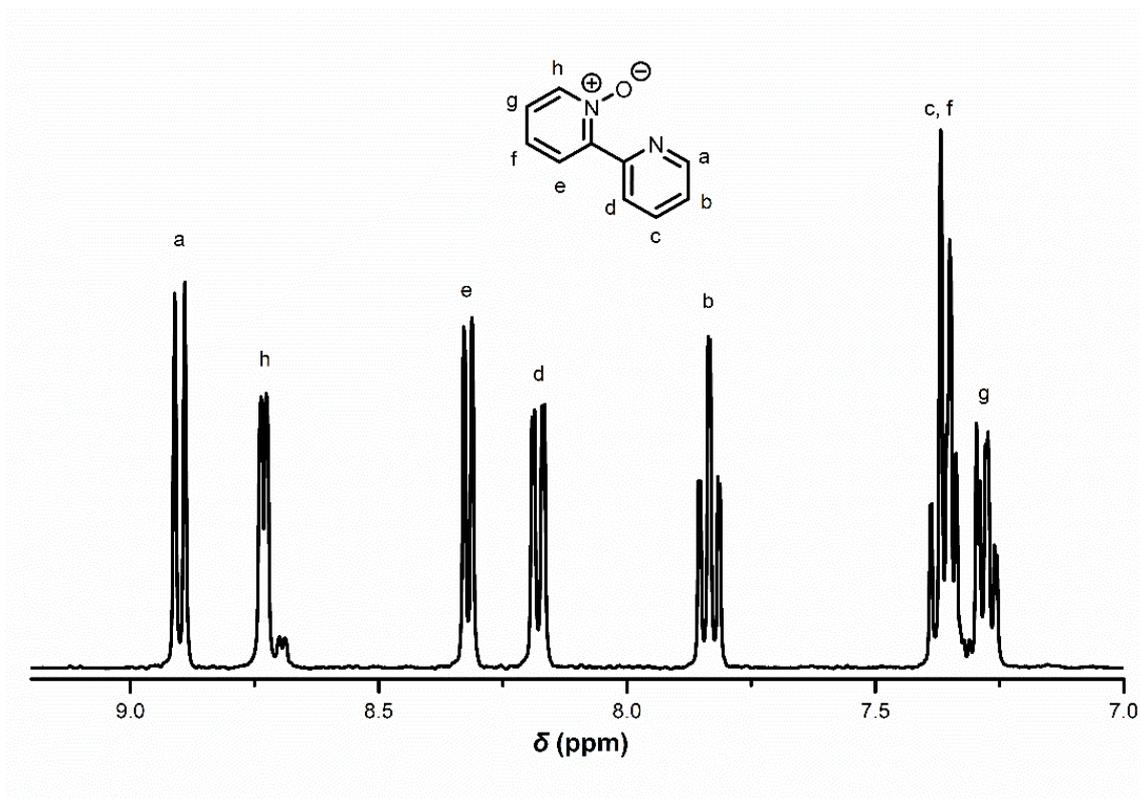
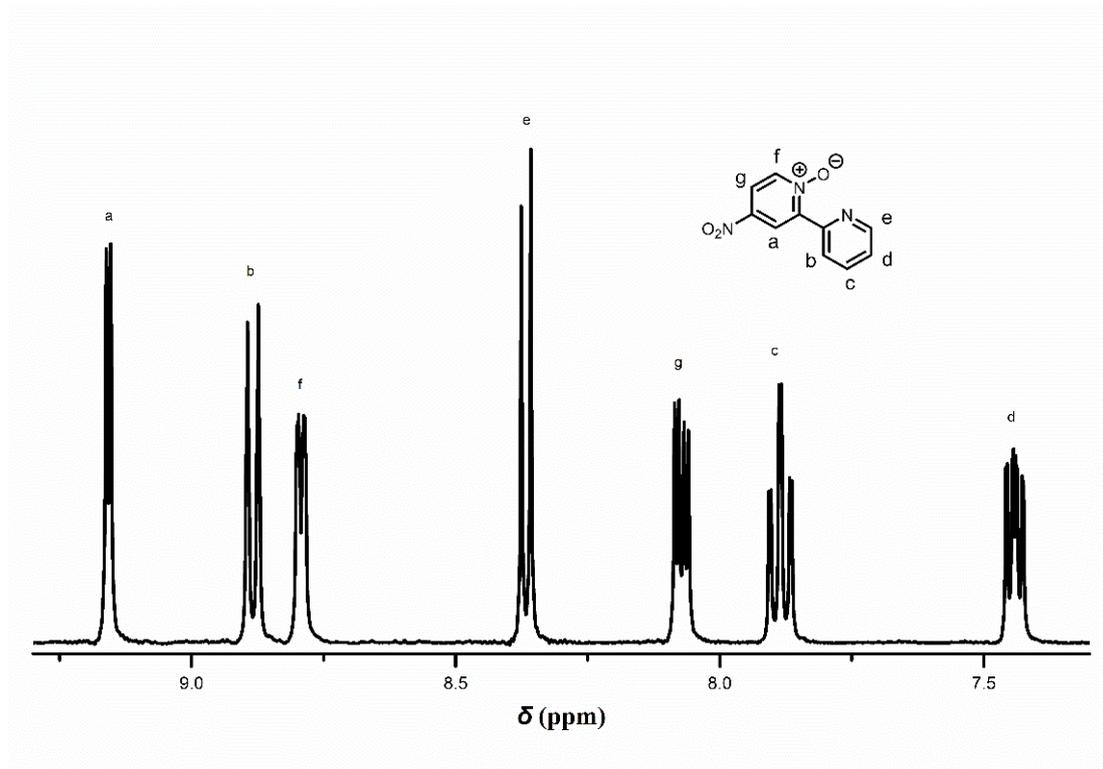**Fig. S2** ^{1}H NMR spectrum of 2,2'-bipyridine-*N*-oxide in CDCl$_3$.

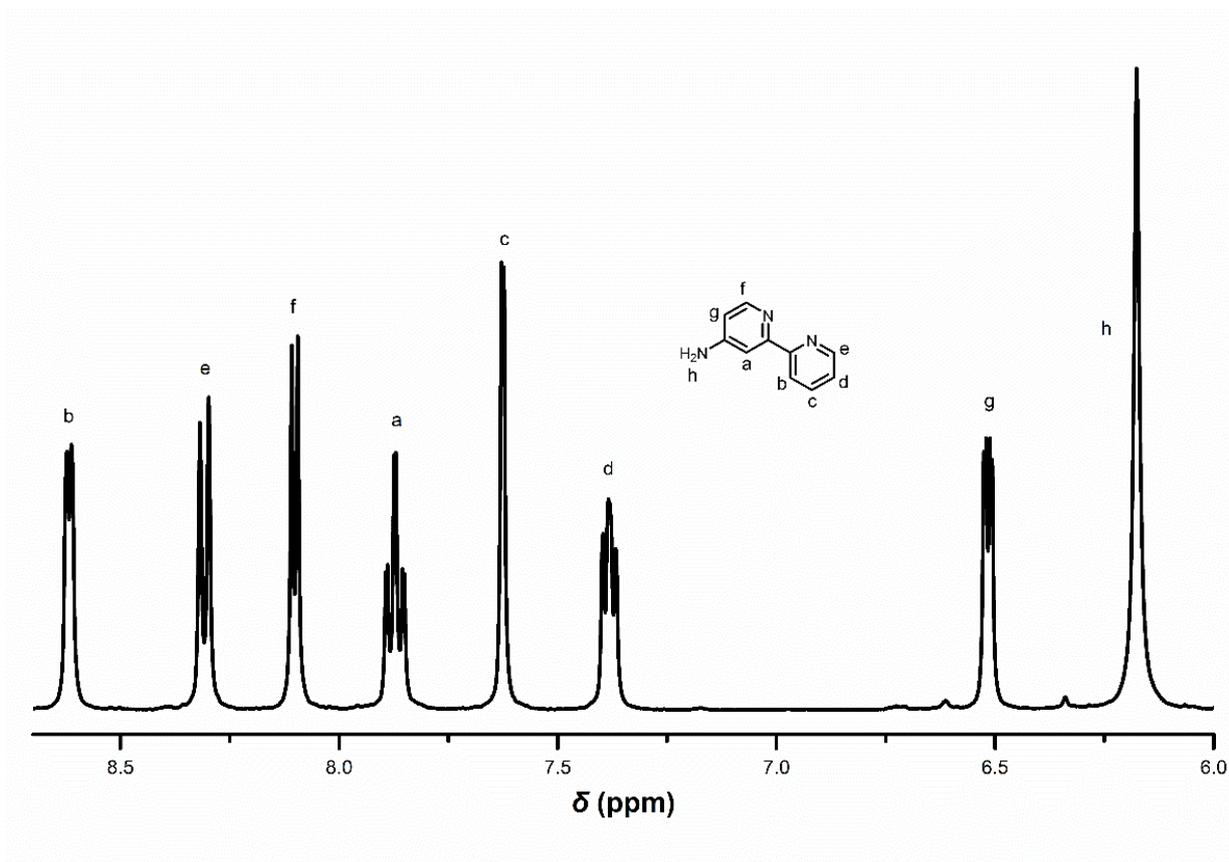**Fig. S3** ^{1}H NMR spectrum of 4-nitro-2,2'-bipyridine-*N*-oxide in CDCl$_3$.

Fig. S4 ^{1}H NMR spectrum of 4-amino-2,2'-bipyridine in CDCl$_3$.
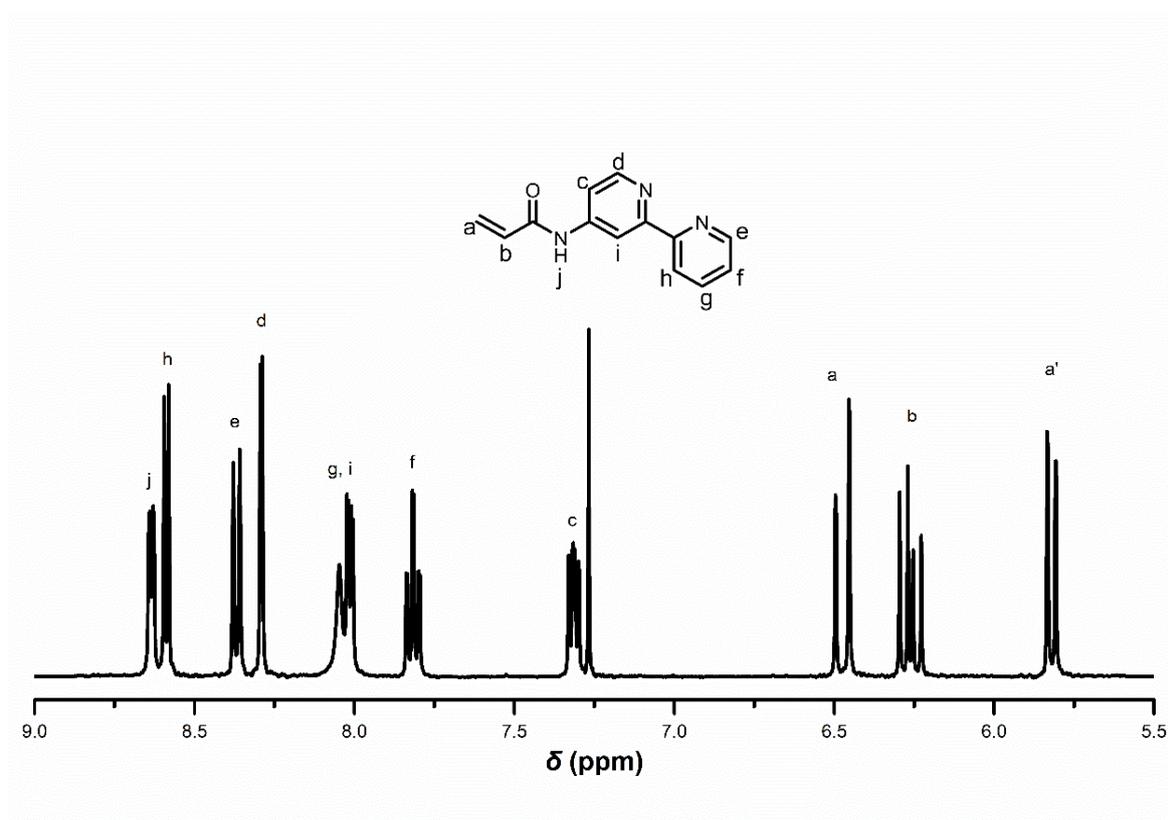

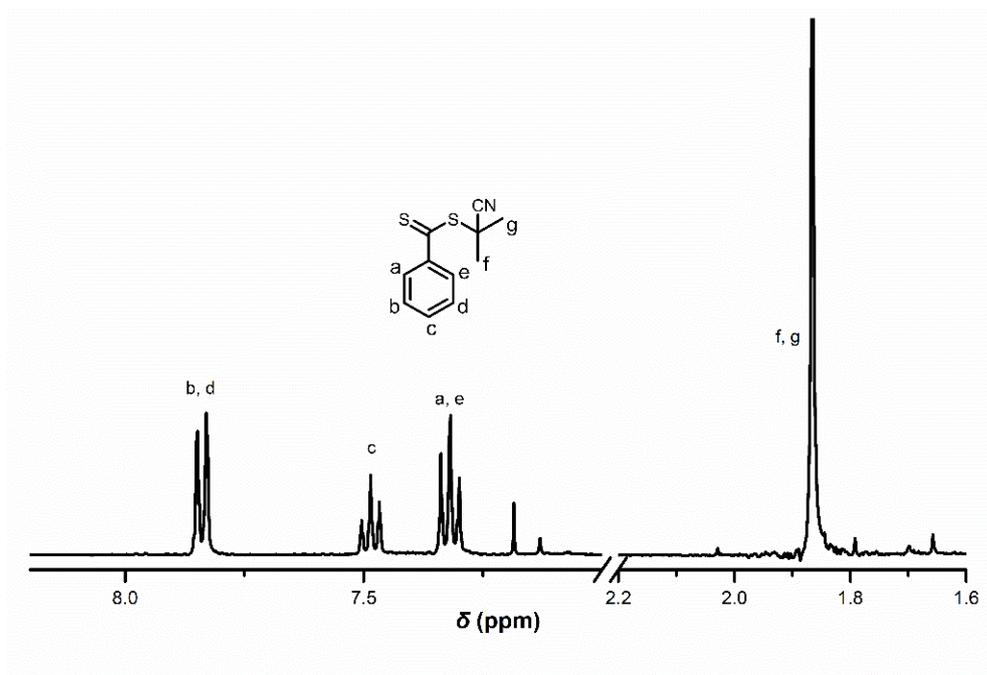**Fig. S5** ^{1}H NMR spectrum of *N*-([2,2'-bipyridin]-4-yl)acrylamide in CDCl$_3$.
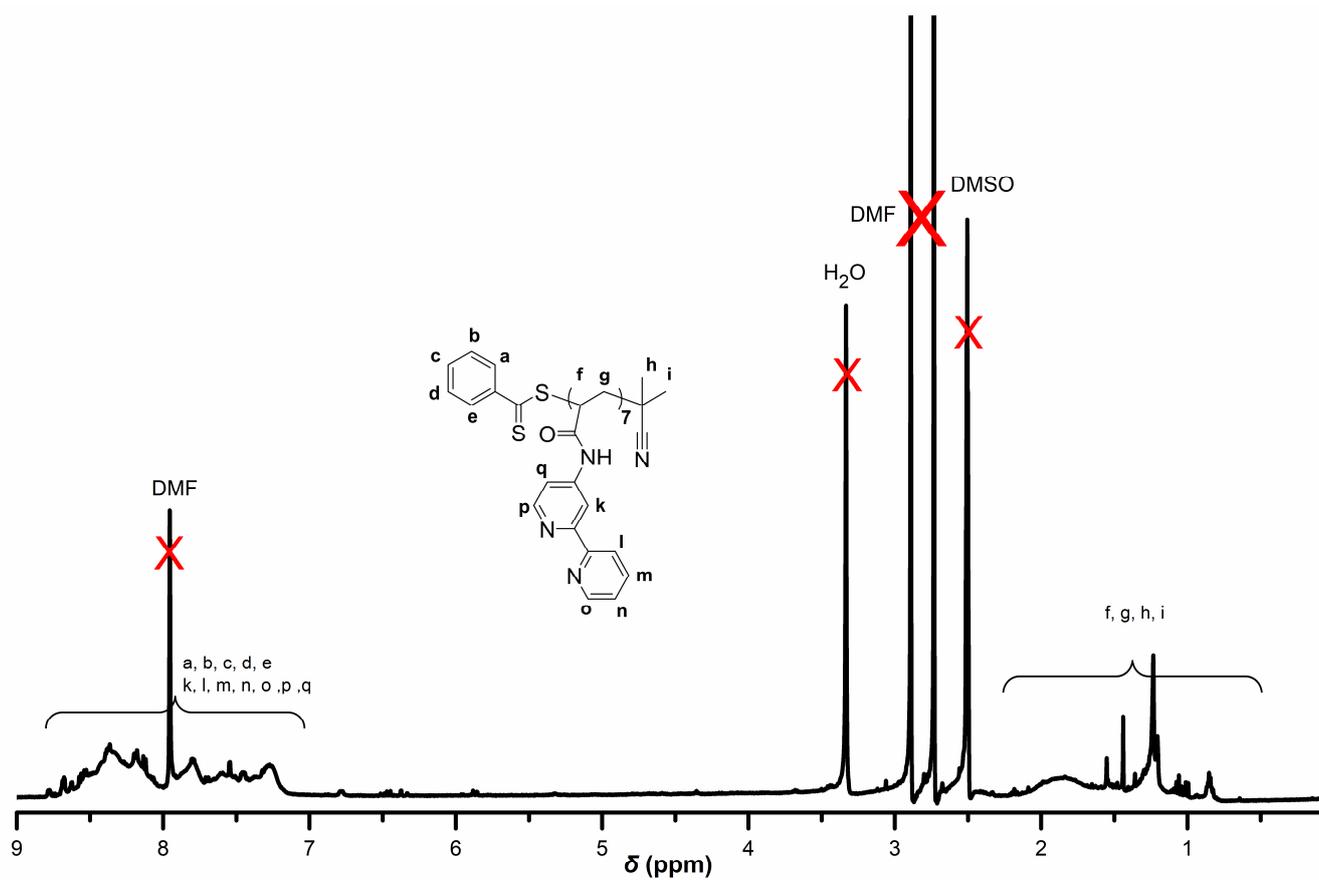
Fig. S6 ^{1}H NMR spectrum of CPDB.

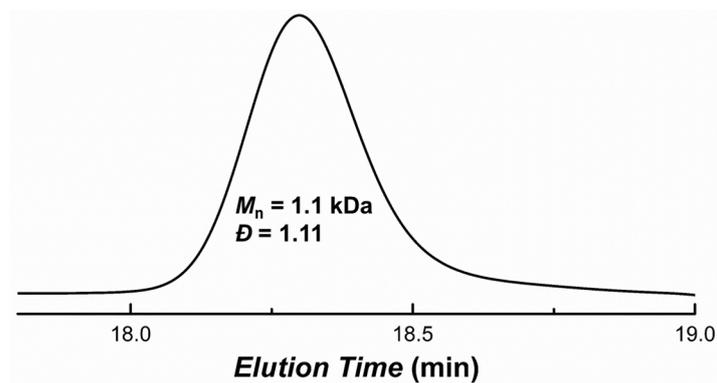**Fig. S7** ^{1}H NMR spectrum of PBPy in DMSO-d_6.
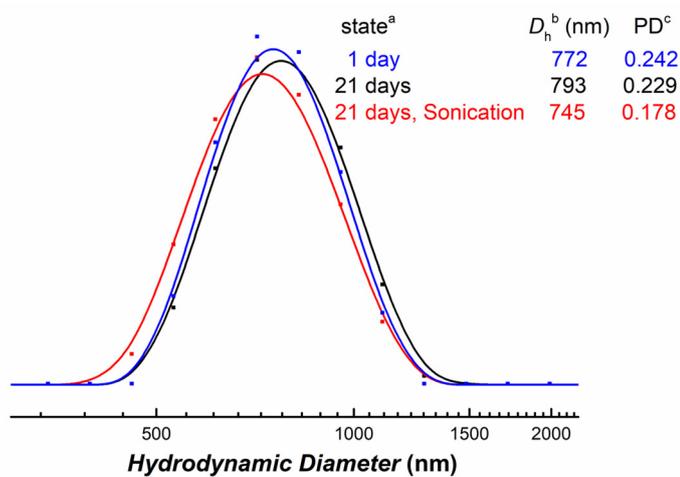
Fig. S8 DMF SEC trace of PBPy.

Fig. S9 DLS results of nanobowls self-assembled at 20 °C, pH 6.0 and 0.2 mg mL^{-1} of initial PBPy concentration in THF. [a] The nanobowls were reserved until DLS measurement; sonication means the aqueous solution of nanobowls was ultrasonicated before the tests. [b] The Z-average diameter of nanobowls. [c] The polydispersity of nanobowls.
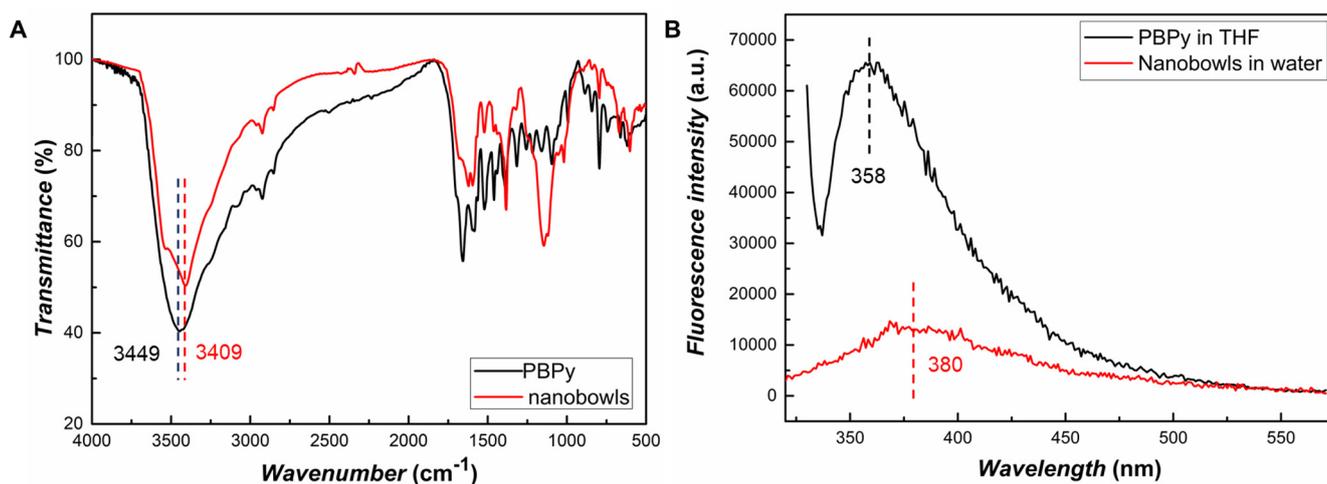
Fig. S10 Characterization of noncovalent interactions during the self-assembly of PBPy. (A) FT-IR spectra of PBPy homopolymer and corresponding freeze-dried powder of nanobowls. (B) Fluorescence spectra of THF solution of PBPy and aqueous solution of nanobowls self-assembled from PBPy. $C_{ini} = 0.2$ mg·mL^{-1}, the excitation wavelength of PBPy was 300 nm, the excitation wavelength of nanobowls was 325 nm.
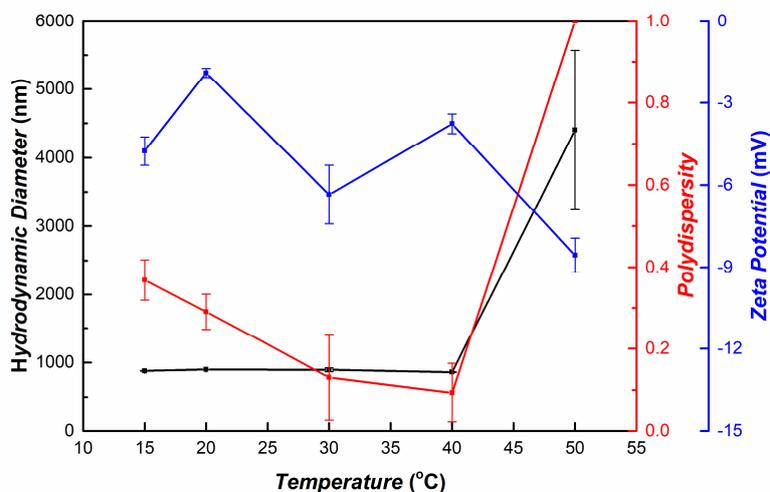

Fig. S11 DLS results and Zeta potential of nanobowls self-assembled from PBPy at different temperatures (T_s). Nanobowls were assembled in water at pH 7.0 and dialyzed in water at pH 7.0; $C_{ini} = 0.2$ mg mL^{-1}; the error bars on the data correspond to the standard deviation of D_h, PD and Zeta potential, and each sample was measured for 3 times; the accuracy of Zeta potential measured by Malvern ZS90 is 3.0 mV.
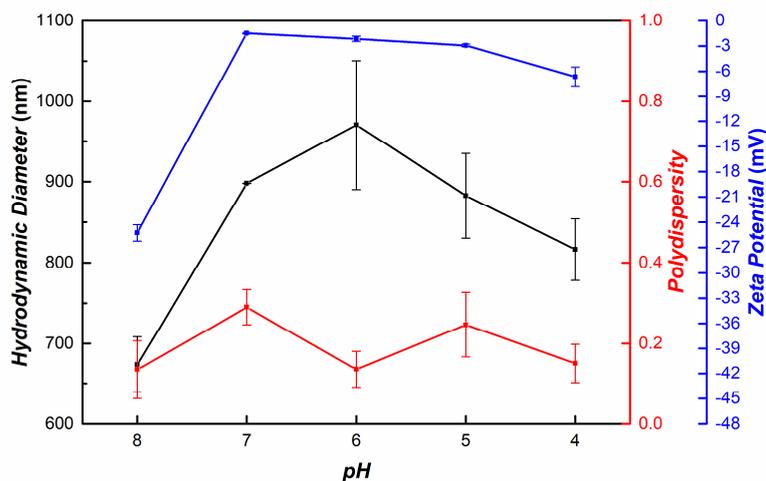
Fig. S12 DLS results and Zeta potential of nanobowls self-assembled from PBPy at different pHs. Nanobowls were dialyzed in water at the same pH; $C_{ini} = 0.2$ mg mL^{-1}; temperature was 20 °C; the error bars on the data correspond to the standard deviation of D_h, PD and Zeta potential, and each sample was measured for 3 times; the accuracy of Zeta potential measured by Malvern ZS90 is 3 mV.

Table S1 The mean values of nanobowl dimensions self-assembled at different T_ss

Temperature (°C)	D (nm) [a]	H/D [b]	W/D [c]
15	683	0.511	0.596
20	807	0.492	0.686
30	878	0.558	0.757
40	908	0.546	0.754

[a] D is the diameter of the nanobowl. [b] H is the depth of the concave. [c] W is the width of the opening. The mean value of was averaged over 5 measurements.

Table S2 The mean values of nanobowl dimensions self-assembled at different pHs

pH	D (nm) [a]	H/D [b]	W/D [c]
4.0	1382	0.595	0.728
5.0	806	0.623	0.524
6.0	830	0.581	0.575
7.0	793	0.492	0.686
8.0	802	0.501	0.583

[a] D is the diameter of the nanobowls. [b] H is the depth of the concave. [c] W is the width of the opening. The mean value was averaged over 5 measurements.
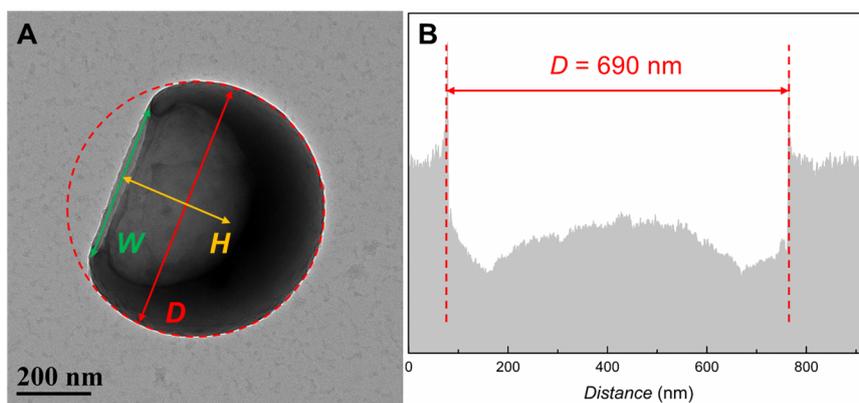
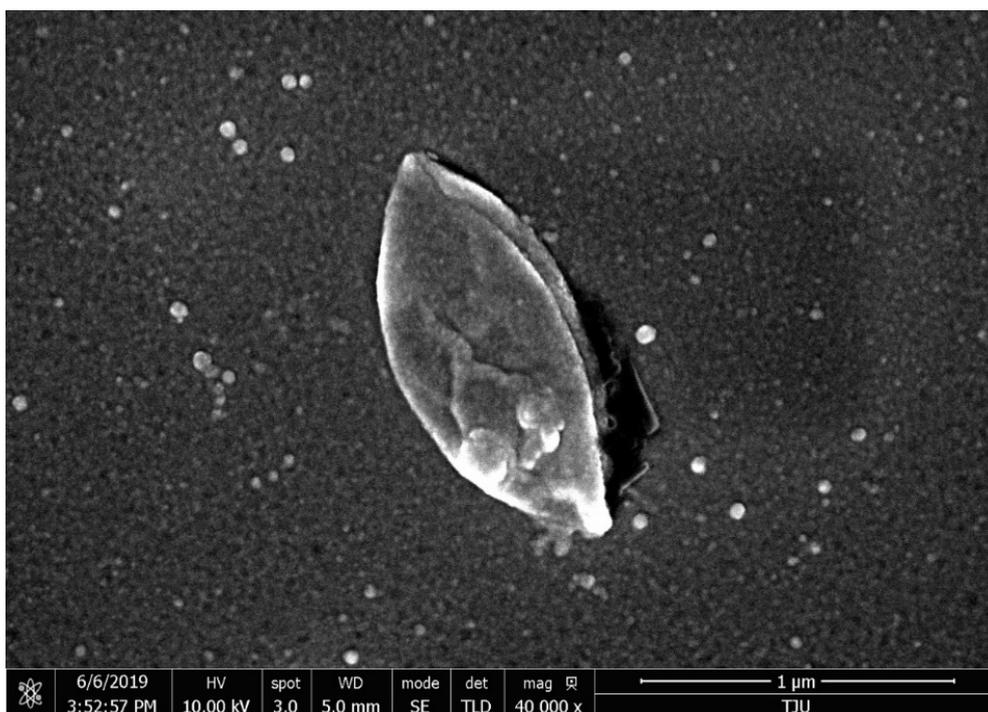**Fig. S13** TEM intensity profiles (B) for measuring *D*, *W* and *H* of a nanobowl illustrated in A.

.Fig. S14 SEM image of a collapsed vesicle self-assembled at a molar ratio of Fe^{2+} : BPy = 1 : 8.

5 References

1 X. Zhou, T. Zhang, C. W. Abney, Z. Li and W. B. Lin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18475-18479.