Electronic Supplementary Information

Gathering nanorings via Fe^{2+}-bipyridine coordination

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Contents:

1. General methods

All the starting materials were obtained from Adamas or Sangon Biotech. Commercially available reagents were used without further purification, unless noted otherwise. All chemicals were reagent grade or better. ^{1}H NMR and ^{13}C NMR spectra were performed on a 400 MHz Bruker AV 400. ESI mass spectra were obtained on a Finnigan LCQ Advantage ion trap mass spectrometer (ThermoFisher Corporation) equipped with a standard ESI source. HPLC analyses were performed on an Agilent 1200 HPLC system equipped with a G1322A pump and in-line diode array UV detector using a YMC-Pack ODS-AM column with CH_3CN (0.1% of TFA) and water (0.1% of TFA) as the eluent. Transmission electron micrograph (TEM) images were obtained on a JEOL 2100F electron microscope, operating at 200 kV. The cryo-dried samples were prepared as following: a copper grid coated with carbon was dipped into the suspension solvent and placed into a vial, which was plunged into liquid nitrogen until no bubbles were apparent. Then water was removed from the frozen specimen by a freeze-drier. UV-vis absorbance spectra were recorded on a lambda 25 UV-visible spectrophotometer (PerkinElmer, America) at room temperature. Fluorescence

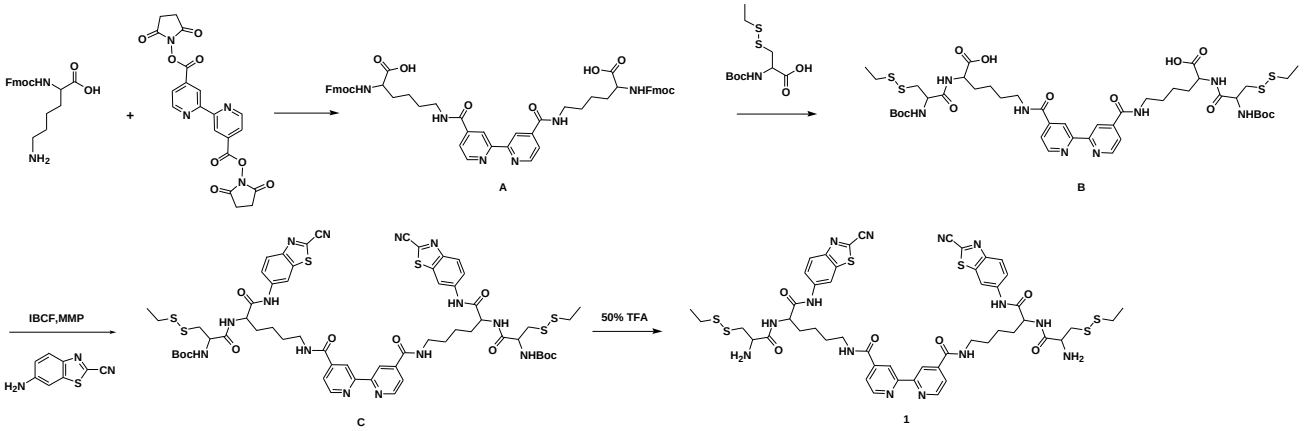
spectra were recorded on a F-4600 fluorescence spectrophotometer (Hitachi High-Techonologies Corporation, Japan) with excitation wavelengths set to 320 nm. Dynamic light scattering (DLS) was measured on a Zeta Sizer Nano Series (Malvern Instruments).

2. Chemical syntheses and characterizations of precusors and 1

The preparations of compound **1** was described as below；2-cyano-6-aminobenzothiazole (CBT) was synthesized following the literature method.[1]

Preparation of **1**.

Scheme S1. Synthetic route for compound ***1***.



*Synthesis of **A***:

Fmoc-Lys-OH-HCl (1.104 g, 2.5 mmol) was dissolved in 15 mL of dry DMF and then DIEA (400 μL, 2.35 mmol) was added. 4,4'-dicarboxysuccinimidyl-2,2'-bipyridine (438 mg, 1 mmol) in dry DMF was added dropwise into the solution and stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the reaction mixture was subjected to HPLC purification to yield pure compound **A**

(740 mg, 78%). MS of **A**: calc. for $C_{54}H_{53}N_6O_{10,}$ [$(M+H)^+$]: 945.38; obsvd. ESI-MS: m/z 945.42 (Figure S1).

*Synthesis of **1***:

Compound **B** (**B**, 103 mg, 0.1 mmol) was prepared by solid phase peptide synthesis (SPPS). The isobutyl chloroformate (8.7 µL, 0.12 mmol) was added to a mixture of **B** (180 mg, 0.1 mmol) and 4-methylmorpholine (MMP, 8.5 µL, 0.15 mmol) in THF (1.5 mL) at 0 °C under N_2 and the reaction mixture was stirred for 20 min. The solution of 2-cyano-6-aminobenzothiazole (CBT, 18 mg, 0.1 mmol) was added to the reaction mixture and further stirred for 1 h at 0 °C then overnight at room temperature. The pure product **C** (47 mg, 35%) was obtained after HPLC purification. The Boc protecting groups of **C** were cleaved with 95% TFA in CH_2Cl_2 for 3 hrs in the presence of 1% triisopropylsilane. The pure product **1** (20 mg, 50%) was obtained after HPLC purification. MS of **1**: calc. for $C_{50}H_{57}N_{14}O_6S_6$, [$(M+H)^+$]: 1141.2910; obsvd. HR-ESI-MS: m/z 1141.2912 (Figure S3). ^{1}H NMR of **1** (CD_3OD, 400 MHz, Figure S4) δ (ppm): 8.66 (d, J = 4.0 Hz, 2 H), 8.59 (d, J = 4.0 Hz, 2 H), 8.53 (s, 2 H), 4.67 (m, 2 H), 4.22 (m, 2 H), 3.46 (br, 4 H), 3.07 (br, 4 H), 2.75 (br, 4H), 2.00 (br, 4H), 1.75 (br, 4H), 1.69 (br, 4H), 1.30 (m, 6 H). ^{13}C NMR of compound **1** (100 MHz, d_6-DMSO, Figure S5) δ (ppm):170.47, 166.90, 164.42, 155.36, 149.82, 147.68, 142.87, 139.17, 136.60, 135.07, 124.76, 121.80, 120.72, 118.10, 113.48, 111.38, 53.90, 51.17, 31.80, 31.26, 28.65, 22.73, 13.97.

3. Supporting figures and tables

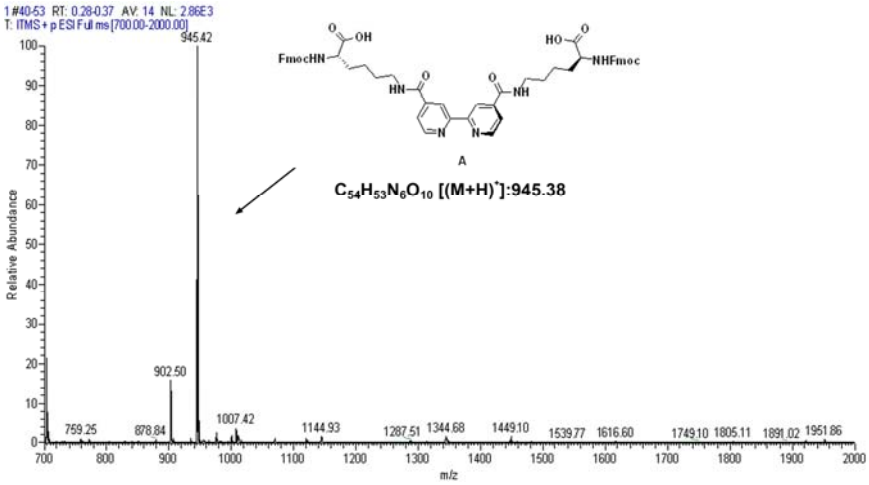


Figure S1. ESI-MS spectrum of compound **A**.

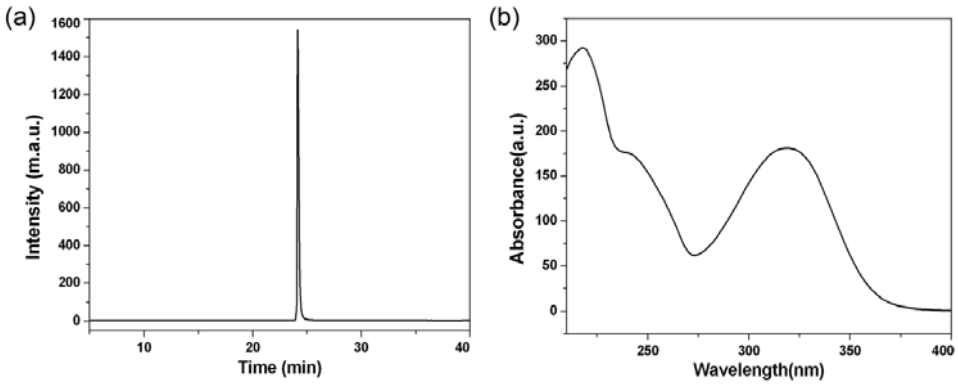


Figure S2. HPLC trace (a) and UV-vis spectrum (b) of compound **1** in distilled water, respectively.

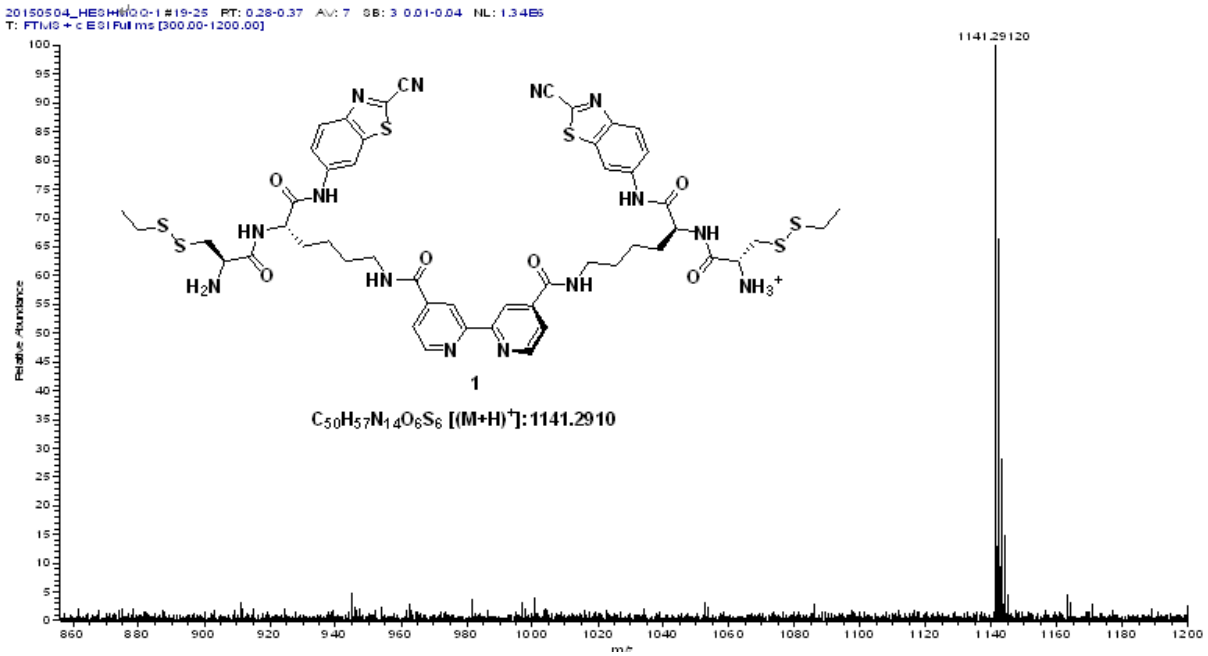


Figure S3. HR-ESI/MS spectrum of **1**.

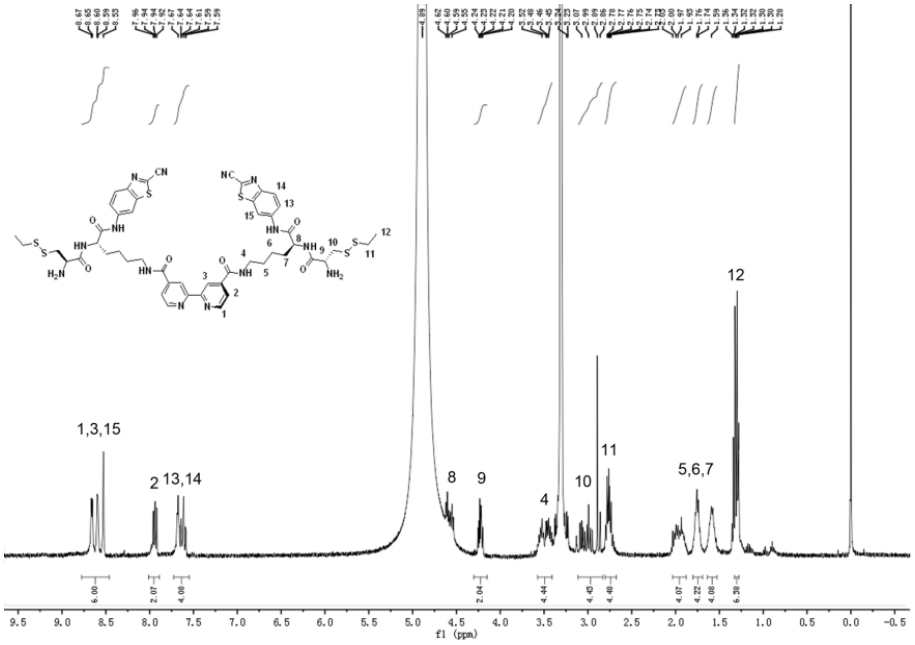


Figure S4. ^{1}H NMR spectrum of **1**.

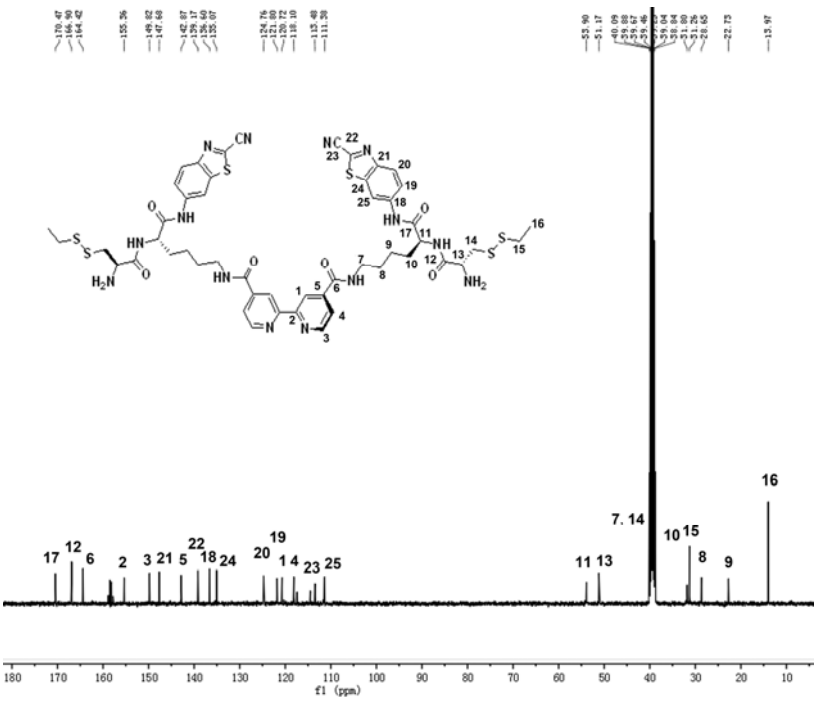


Figure S5. ^{13}C NMR spectrum of **1**.

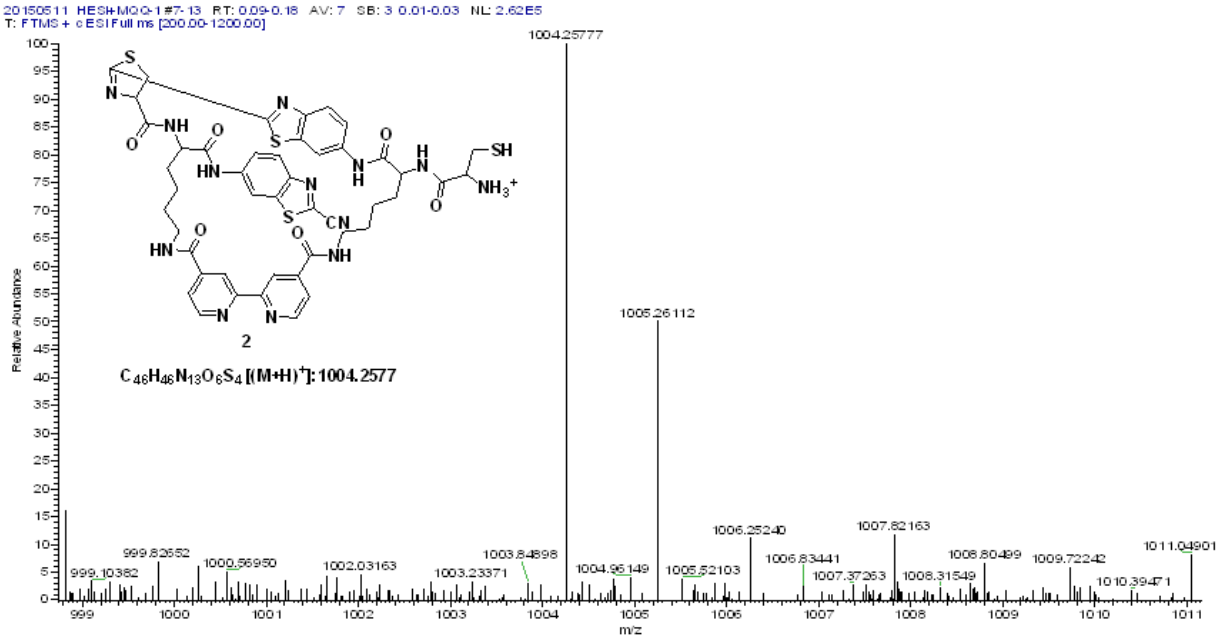


Figure S6. HR-ESI/MS spectrum of HPLC peak at retention time of 21.5 min in Figure 2a.

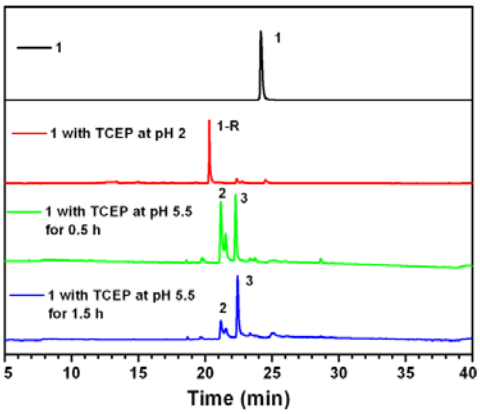


Figure S7. HPLC traces of **1** (black), 100 μM of **1** with 4 equiv. of TCEP at pH 2 for 0.5 h (red), 100 μM of **1** with 4 equiv. of TCEP at pH 5.5 for 0.5 h (green), 100 μM of **1** with 4 equiv. of TCEP at pH 5.5 for 1.5 h (blue). Absorbance: 320 nm.

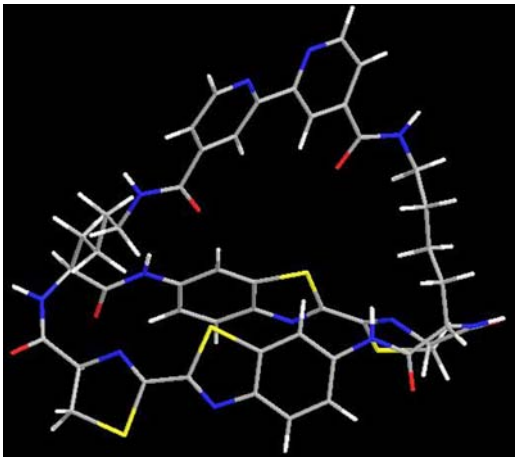


Figure S8. Theoretically optimized molecular structure of **3**.

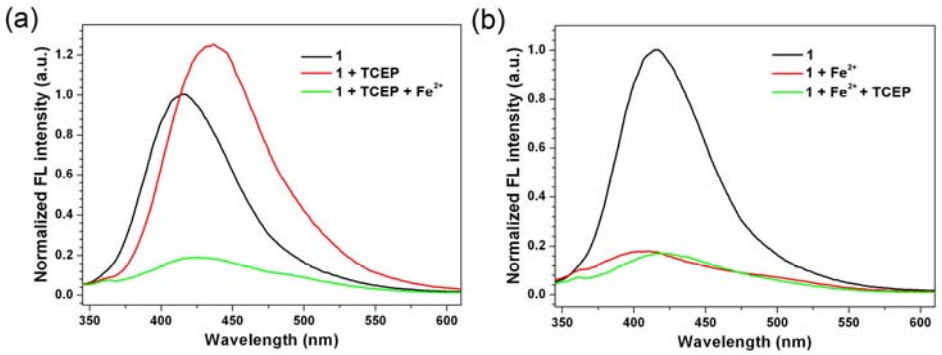


Figure S9. (a) Fluorescence spectra of **1** at 100 μM (black), 100 μM **1** reduced by 400 μM TCEP at pH 5.5 for 1.5 h (red), 100 μM **1** reduced by 400 μM TCEP for 1.5 h and then treated with 1 mM Fe^{2+} at pH 5.5 for 1 h (green). Excitation: 320 nm. (b) Fluorescence spectra of **1** at 100 μM (black), 100 μM **1** treated with 1 mM Fe^{2+} at pH 5.5 for 1 h (red), 100 μM **1** treated with 1 mM Fe^{2+} for 1 h and then reduced by 400 μM TCEP at pH 5.5 for 1.5 h (green). Excitation: 320 nm.

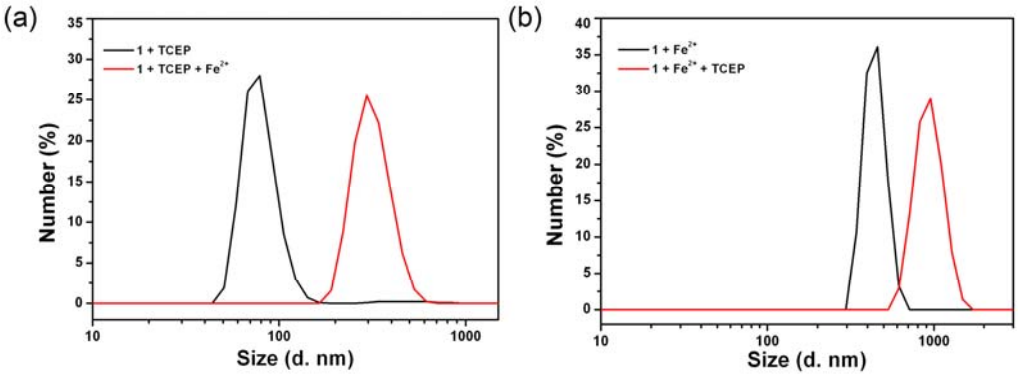


Figure S10. (a) Dynamic light scattering (DLS) analysis of particles-size distribution of 100 μM **1** incubated with 400 μM TCEP at pH 5.5 and room temperature for 1.5 h (black), 100 μM **1** incubated with 400 μM TCEP at pH 5.5 and room temperature for 1.5 h and then treated with 1 mM Fe^{2+} for another 1 h (red). (b) Dynamic light scattering (DLS) analysis of particles-size distribution of 100 μM **1** incubated with

1 mM Fe^{2+} at pH 5.5 and room temperature for 1 h (black), 100 μM **1** incubated with 1 mM Fe^{2+} at pH 5.5 and room temperature for 1 h and then treated with 400 μM TCEP for another 1.5 h (red).

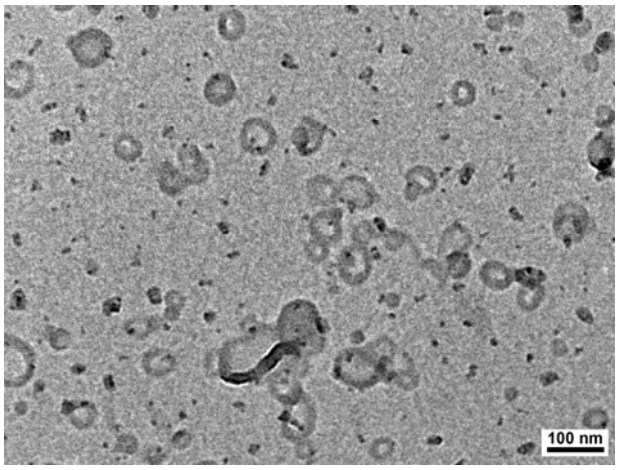


Figure S11. Low magnification of TEM images of nanorings in the reaction mixture of 100 μM **1** treated with 400 μM TCEP at pH 5.5 for 1.5 h.

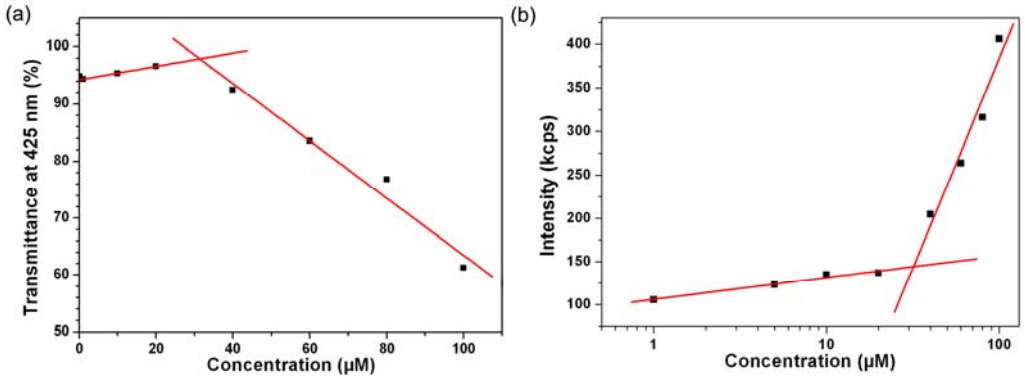


Figure S12. (a) Concentration-dependent optical transmittance at 425 nm of **1** treated with 4 equiv. of TCEP in water at pH 5.5. (b) Concentration-dependent DLS at 633 nm of **1** treated with 4 equiv. of TCEP in water at pH 5.5.

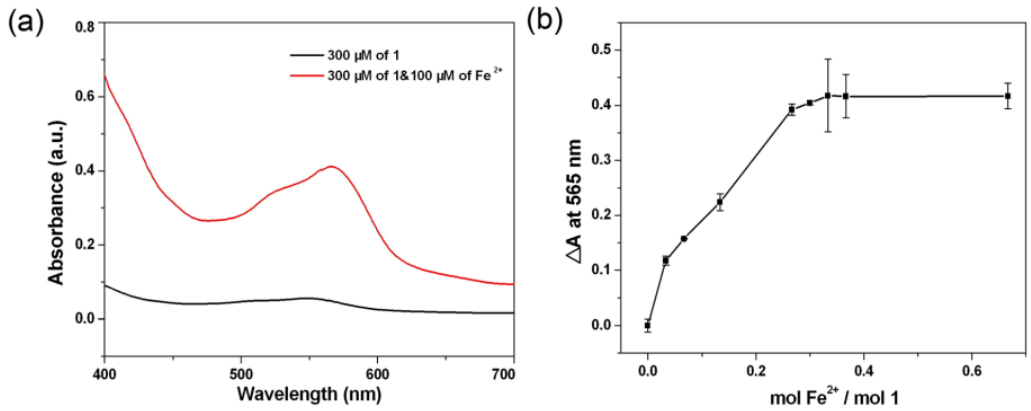


Figure S13. (a) UV-vis spectra of 300 μM **1** (black) and 300 μM **1** with 100 μM Fe^{2+} (red), respectively. (b) UV-vis titration of 300 μM **1** with Fe^{2+}. The addition of Fe^{2+} to a solution of 300 μM **1** generated a maximum absorbance at 565 nm, suggesting the formation of the Fe^{2+}-bipyridine coordination (Figure S13a). Besides, by plotting the absorbance at 565 nm with the molar ration of Fe^{2+} to **1,** a relative molar ratio of 1:3 was achieved, which was consistent with the bidentate coordination of bipyridine to octahedral Fe^{2+} (Figure S13b).

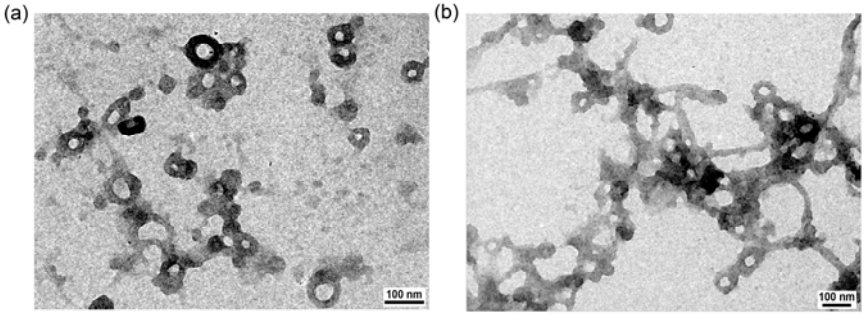


Figure S14. TEM images of nanorings in the reaction mixture of 100 μM **1** treated with 400 μM TCEP at pH 5.5 for 1.5 h, followed by addition of 100 μM Fe^{2+} (a), 10 mM Fe^{2+} (b) and then incubated for 1 h.

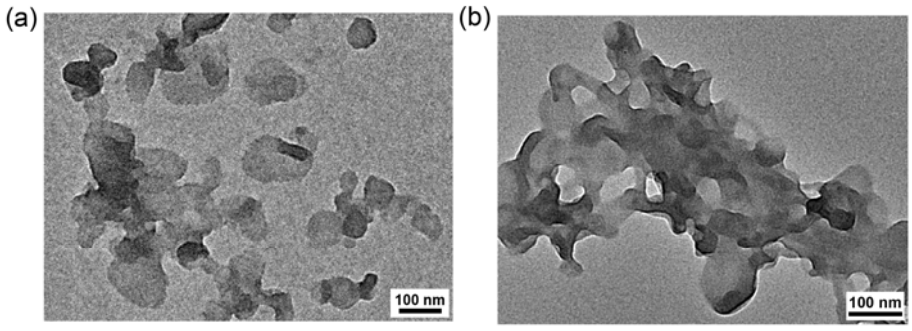


Figure S15. TEM images of the amorphous structures in the mixture of 100 μM **1** treated with 1 mM Fe^{2+} (a), 100 μM **1** treated with 1 mM Fe^{2+} and then reduced by 400 μM TCEP (b).

Table S1. HPLC condition for the purification of precusors and **1**.

Time (minute)	Flow (ml/min.)	H_2O %	CH_3CN%
0	3.0	30	70
3	3.0	30	70
35	3.0	0	100
37	3.0	0	100
38	3.0	30	70
40	3.0	30	70

4. References

1 E. H. White, H. Worther, H. H. Seliger and W. D. Mcelroy, *J. Am. Chem. Soc.*, 1966, **88**, 2015-2019.