Supporting Information

Supramolecular polymers bearing disulfide bonds

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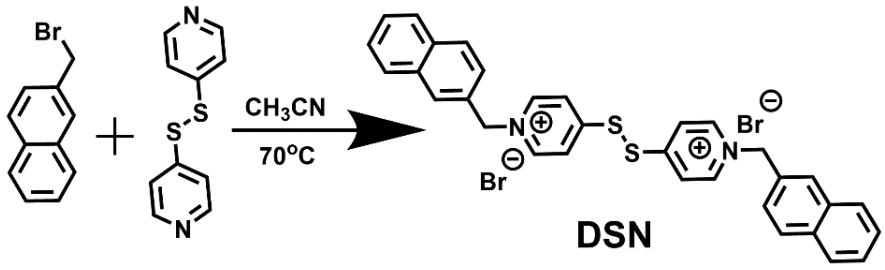
1. Experimental Section

1.1 Materials.

4-Dithiothreitol (DTT, 99%) was purchased from ACROS. 2-Bromomethyl naphthalene (96%) and 4, 4'-dithiopyridine (97%) were purchased from J&K chemical. L-glutathione (reduced, GSH, 98%) was purchased from SIGMA-ALDRICH. Diethyl ether (anhydrous, 99.7%) and hydrogen peroxide 30% were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile (99%) was purchased from Beijing chemical works. Cucurbit[8]uril (CB[8]) came from Prof. Oren. A. Scherman, University of Cambridge.

1.2 Synthesis of 4, 4'-disulfanediylbis(1-(naphthalen-2-ylmethyl)pyridin-1-ium) bromide.

4, 4'-Dithiopyridine (0.22 g, 1.0 mmol) and 2-bromomethyl naphthalene (1.0 g, 4.5 mmol) were dissolved in acetonitrile (60 ml). Then, the mixture was stirred at 80 ^{o}C for 12 h. After that, the solution was added dropwise into 500 ml diethyl ether with ultrasonic for twice, then it was filtered to obtain the yellow precipitate 4, 4'-disulfanediylbis(1-(naphthalene-2-ylmethyl)pyridin-1-ium) bromide (DSN, 0.56 g, 85%). ^{1}H NMR (400 MHz, D_2O, ppm) δ: 8.76, 8.74 (4H, H of pyridine, d), 7.96, 7.94 (4H, H of pyridine, d), 7.89-7.34 (14H, H of naphthalene, m), 5.79 (4H, CH_2, s). ^{13}C NMR (400 MHz, D_2O, ppm) δ: 154.6, 144.8, 128.8 (C of pyridine units), 125.9-133.6 (C of naphthalene units), 65.0 (C of CH_2).



Scheme S1 The synthesis of DSN.

1.3 Preparation of supramolecular polymers DSN-CB[8]

The supramolecular polymers (DPS-CB[8]) were fabricated by mixing CB[8] (6.3 mg, 4 μmol) and DPS (2.6 mg, 4 μmol) in 4 mL D_2O. ^1H NMR (400 MHz, D_2O, ppm) δ: 8.98, 8.22 (8H, H of pyridine), 6.70, 6.16 (14H, H of naphthalene), 5.70 (4H, CH_2), 5.52, 5.26, 4.02 (16H, H of CB[8]).

2 Characterizations

The ^1H NMR spectra were recorded on a JEOL JNM-ECA 400 (400 MHz). ESI-mass spectroscopy was carried out on a LTQ LC/MS apparatus. The isothermal titration calorimetry (ITC) experiment was performed by a Microcal VP-ITC apparatus in buffered aqueous solution (pH=4.75) at 298 K. DOSY were carried out with a BRUKER AVANCE 600 NMR spectrometer. Asymmetric Flow Field Flow Fractionation experiments (AsF-FFF) were performed by Wyatt Technology Eclipse 3+ with multi-angle light scattering detector (DAWN HELEOS-II), Ultraviolet and Differential Refraction detector (Optilab rEX). UV-Vis spectra were obtained using a Hitachi U-3010 spectrophotometer.

3.1 The diffusion coefficient of DSN upon adding ADA into the solution of supramolecular polymers.

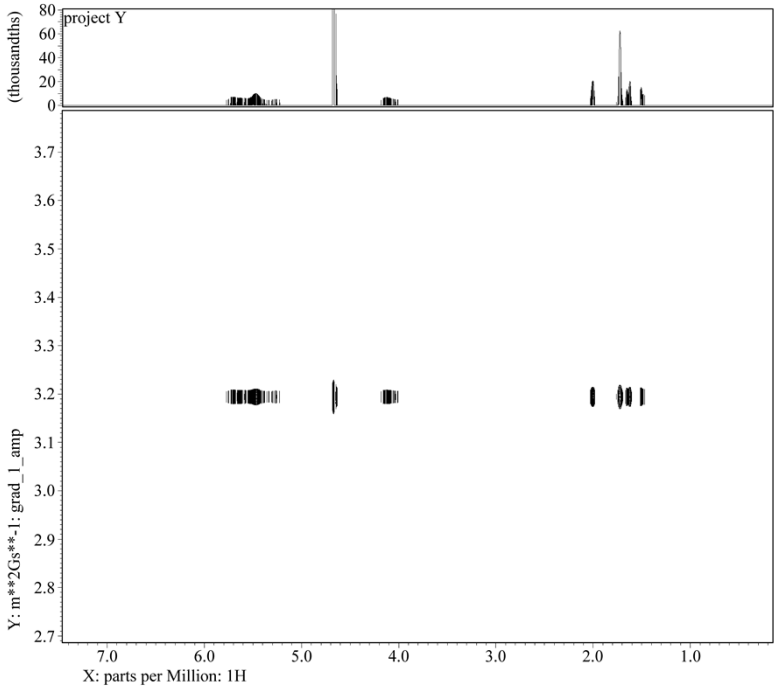


Fig. S1 The diffusion coefficient of supramolecular polymers DSN-CB[8] after adding ADA.

3.2 UV-Vis absorbance of DSN after adding 1.5 equiv GSH into DSN solution with extending the reduction time of GSH.

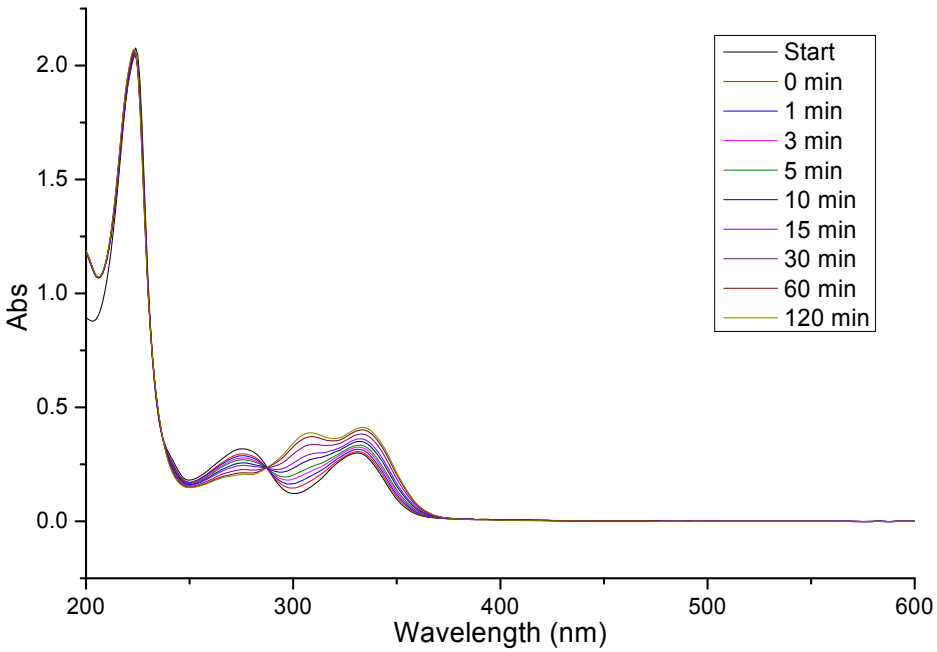


Fig. S2 UV-vis spectra of DSN upon the adding of GSH (1.5 equiv).

3.3 UV-Vis spectra of DSN upon increasing the oxidation time of H_2O_2 (100 equiv)

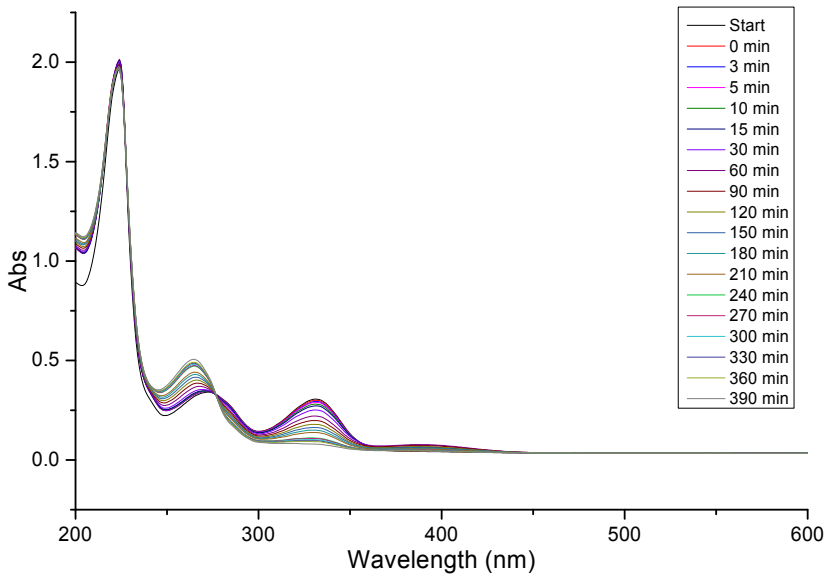


Fig. S3 UV-vis spectra of of DSN upon the adding of H_2O_2 (100 equiv).

3.4 UV-Vis spectra of DSN-CB[8] with extending the reduction time of GSH

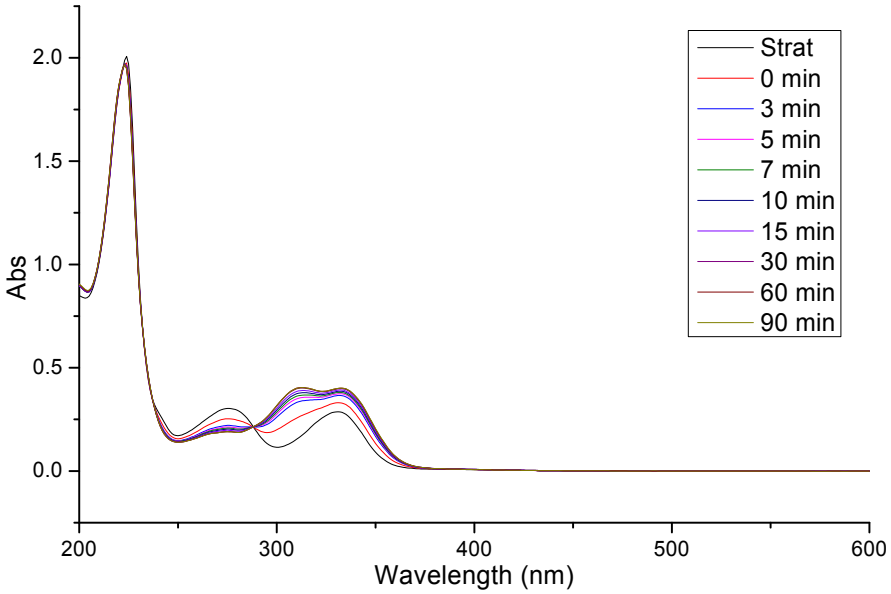


Fig. S4 UV-vis spectra of DSN-CB[8] upon the adding of GSH (1.5 equiv).

3.5 UV-Vis spectra of DSN-CB[8] upon increasing the oxidation time of H_2O_2 (100 equiv)

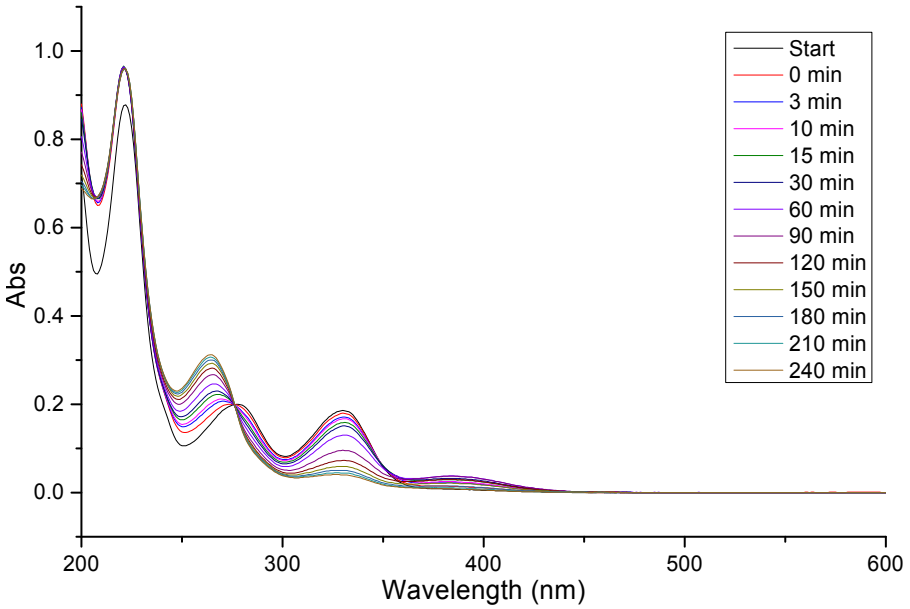


Fig. S5 UV-vis spectra of of DSN-CB[8] upon the adding of H_2O_2 (100 equiv).