SUPPORTING INFORMATION

An acid/base responsive side-chain polyrotaxane system with a fluorescent signal

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Experimental Section

General Methods

^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were acquired on an LCT Premier XE mass spectrometer. UV−Vis absorption spectra and fluorescence spectra were recorded on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1 cm, quartz cells), respectively. Fourier Transform Infrared Spectra (FT-IR spectra) were collected on a Nicolet 380 FT-IR spectrometer in the spectral region of 500-4000 cm^{-1}. SEM images were recorded on a JSM-6360LV apparatus. Confocal fluorescence micrographs were measured on a Nikon A1R confocal laser scanning microscope. Molecular weights of polymer were characterized by gel permeation chromatography performed on an Agilent PL-GPC50. N,N-Dimethylformamide (DMF) was used as an eluent at a flow rate of 1.0 mL min^{-1} at 50 °C. Molecular weights were calculated based on PS standards.

Materials

Chemicals were used as received from Adamas, Acros, Aldrich. All solvents were reagent grade and were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using ^{1}H NMR. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol before use. 2-Cyano-2-butyl dithiobenzoate (CBDB, chain transfer agent) (87mg) was dissolved in 5.0 ml dry DMF and prepared the DMF solution of CBDB (17.4 mg/ml) for use.

Synthesis

The [2]rotaxane compound **1-H** and compound **2** were synthesized according to previous reports [1, 2]. The compound **3** was commercial available without further purification.

Synthesis of Poly-N_3

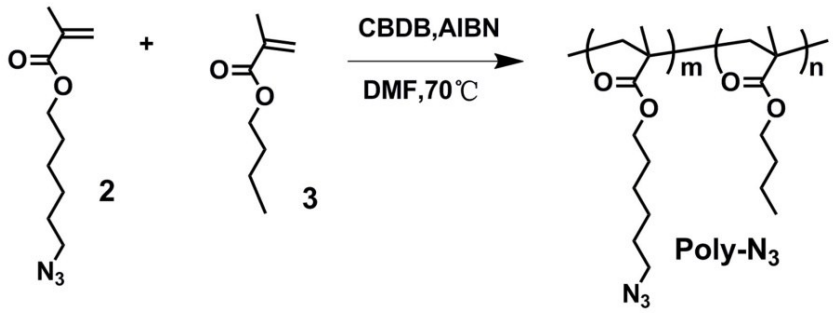

Figure S1. Preparation of **Poly-N_3**

Poly-N_3 was prepared in a closed schlenk reaction flask with a [**2**]:[**3**]:[CBDB]:[AIBN] ratio of 1:20:0.1:0.15. Before the reagent being transferred to the flask, the flask was ventilated with argon for at least 30 min. 100 mg compound **2**, 1.35 g compound g **3**, 0.6 ml DMF solution of CBDB (10.5 mg) and 12 mg AIBN were dissolved in 6.0 ml dry DMF, then the solution was transferred to the schlenk flask and degassed with argon for another 120 min before the polymerization. Then the reaction mixture was reaction under 70 °C for 48 hours. Then the resulting mixture was purified through dialysis against DMF (48 hours) and ethanol (24 hours) to give purified polymer **Poly-N_3** (Mn = 10.05kDa, PDI = 1.39, yield = 83 %)

Synthesis of Poly-1-H

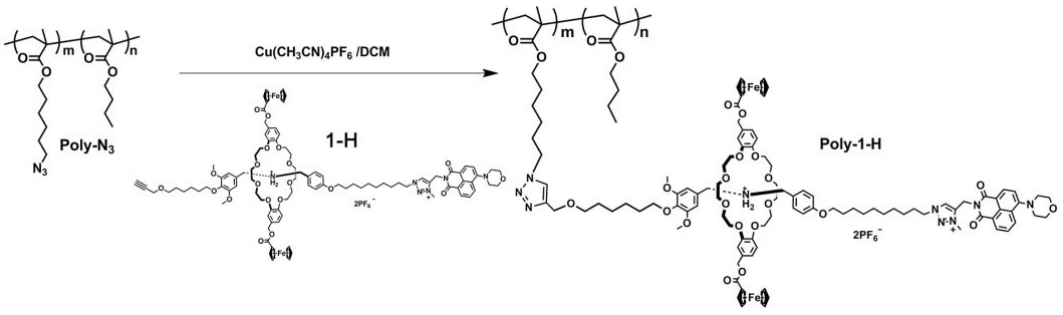

Figure S2. Preparation of **Poly-1-H**

Poly-N_3 (100 mg, 0.01 mmol) and [2]rotaxane compound **1-H (**50 mg, 0.023 mmol) was dissolved in 5 mL dry dichloromethane, $Cu(CH_3CN)_4PF_6$ (10 mg, 0.027 mmol) was added to the solution. The mixture was stirred for 72 hours under Ar atmosphere. The resulting mixture was added into

methanol to precipitate polymeric materials. Precipitation was repeatedly washed with methanol and then through dialysis against DMF (48 hours) and ethanol(24 hours) to ensure that all the unreacted compound **1-H** and other micromolecule compounds were removed to give purified polymer **Poly-1-H** (Mn=21.35kDa, PDI=1.36, yield = 67 %).

The photophysical properties of Poly-1-H

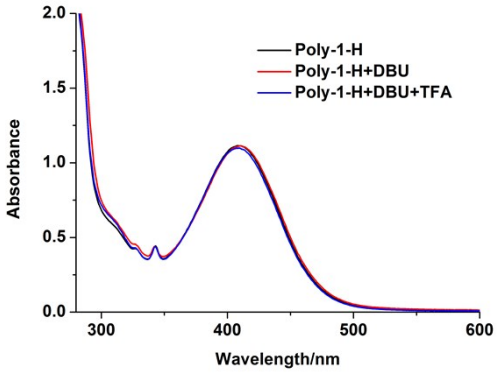

Figure S3. The UV/Vis absorption spectra of a CH_2Cl_2 solution of **Poly-1-H** (0.5 mg/ml) and the mixture obtained after adding excess DBU to the solution of **Poly-1-H**, the mixture obtained after adding excess TFA to the DBU-added solution **Poly-1-H.**

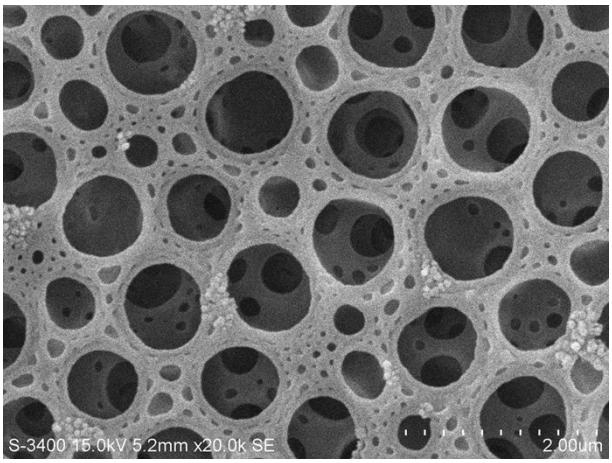

Figure S4. SEM image of solid **Poly-1-H**

Reference:

1. Z.-Q. Cao, Q. Miao, Q. Zhang, H. Li, D.-H. Qu and H. Tian, *Chem. Commun.,* 2015, **51**, 4973-4976.

2. Y. Li and B. C. Benicewicz, *Macromolecules,* 2008, **41,** 7986-7992