

Supplementary Materials

Synthesis and Guest-binding Properties of pH/Reduction Dual-Responsive Cyclophane Dimer

Osamu Hayashida Yudai Tanaka, and Takaaki Miyazaki*

Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma,
Fukuoka 814-0180, Japan

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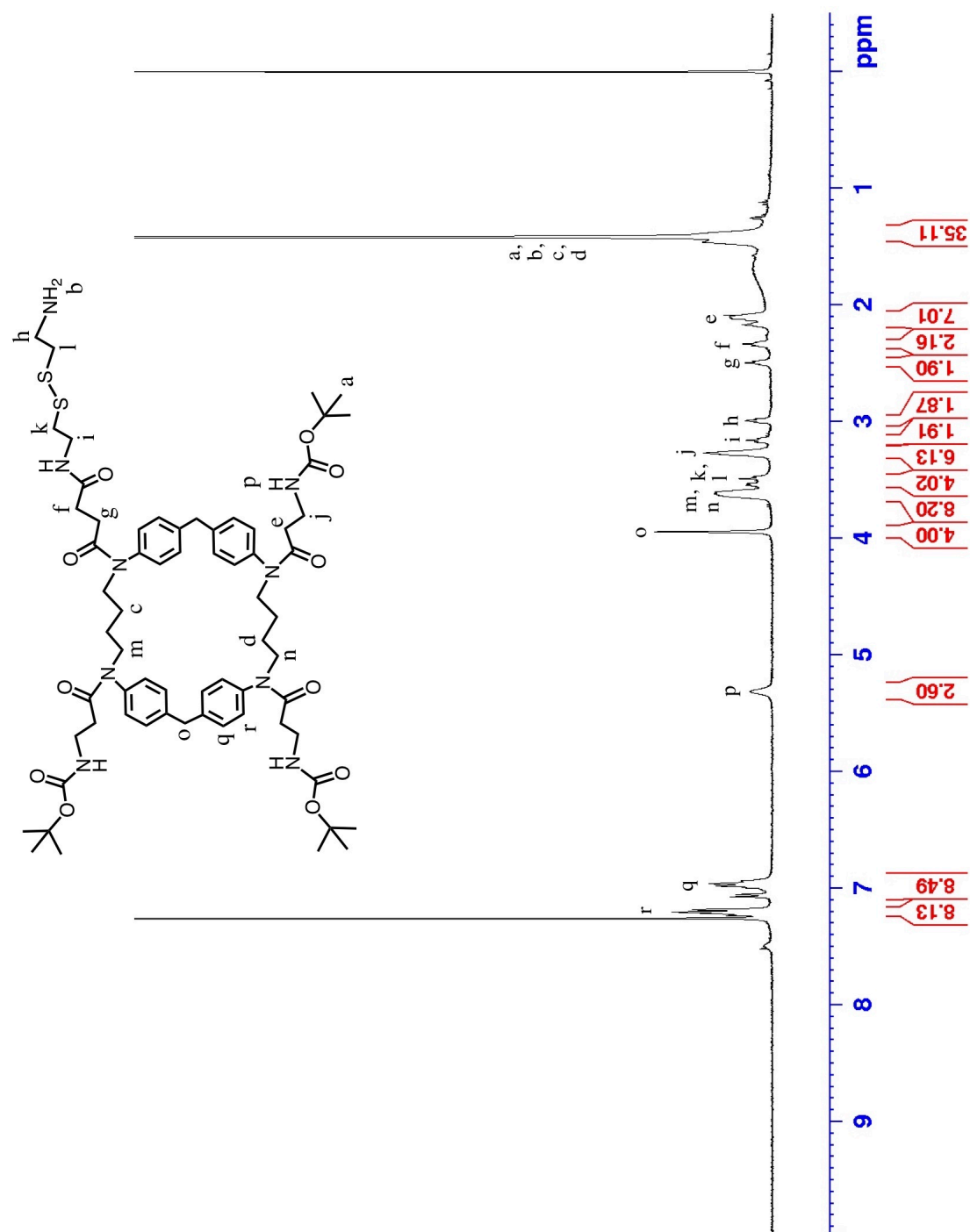


Figure S1. ^1H NMR spectrum of compound 4 (400 MHz, CDCl_3 , 298K).

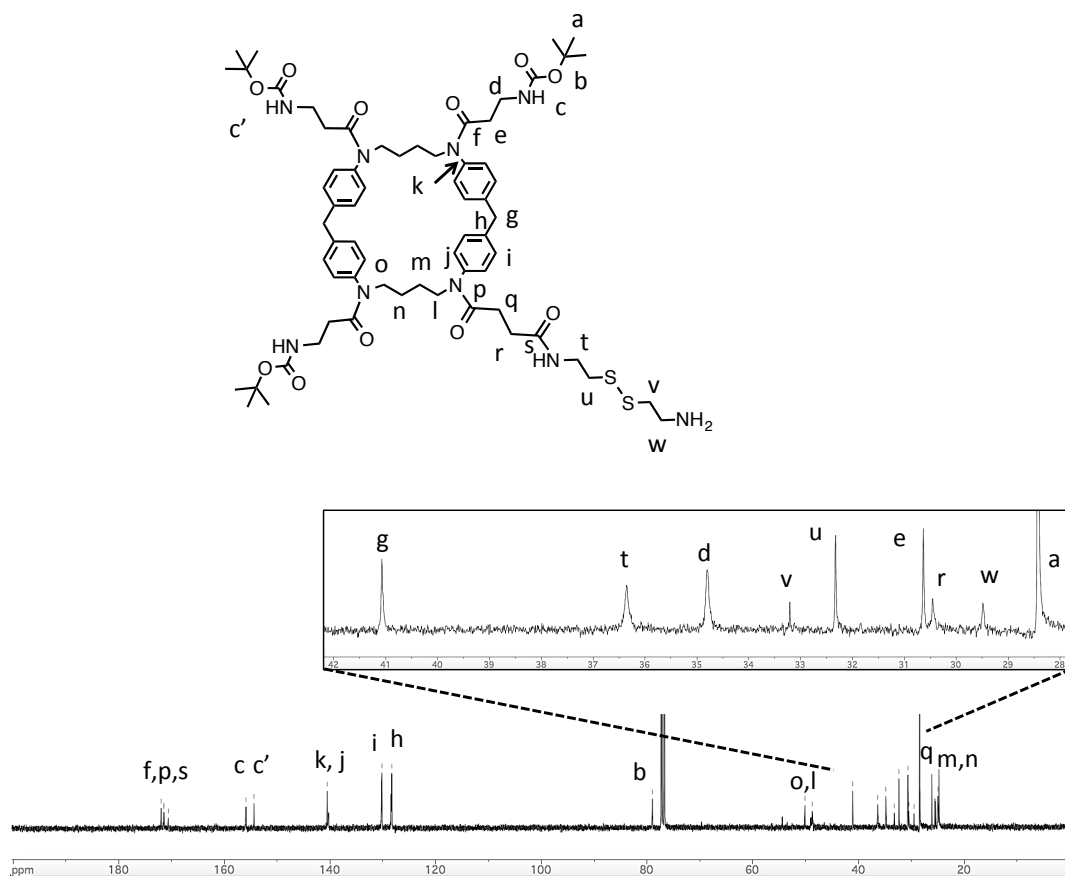


Figure S2. ^{13}C NMR spectrum of compound 4 (100 MHz, CDCl_3 , 298K).

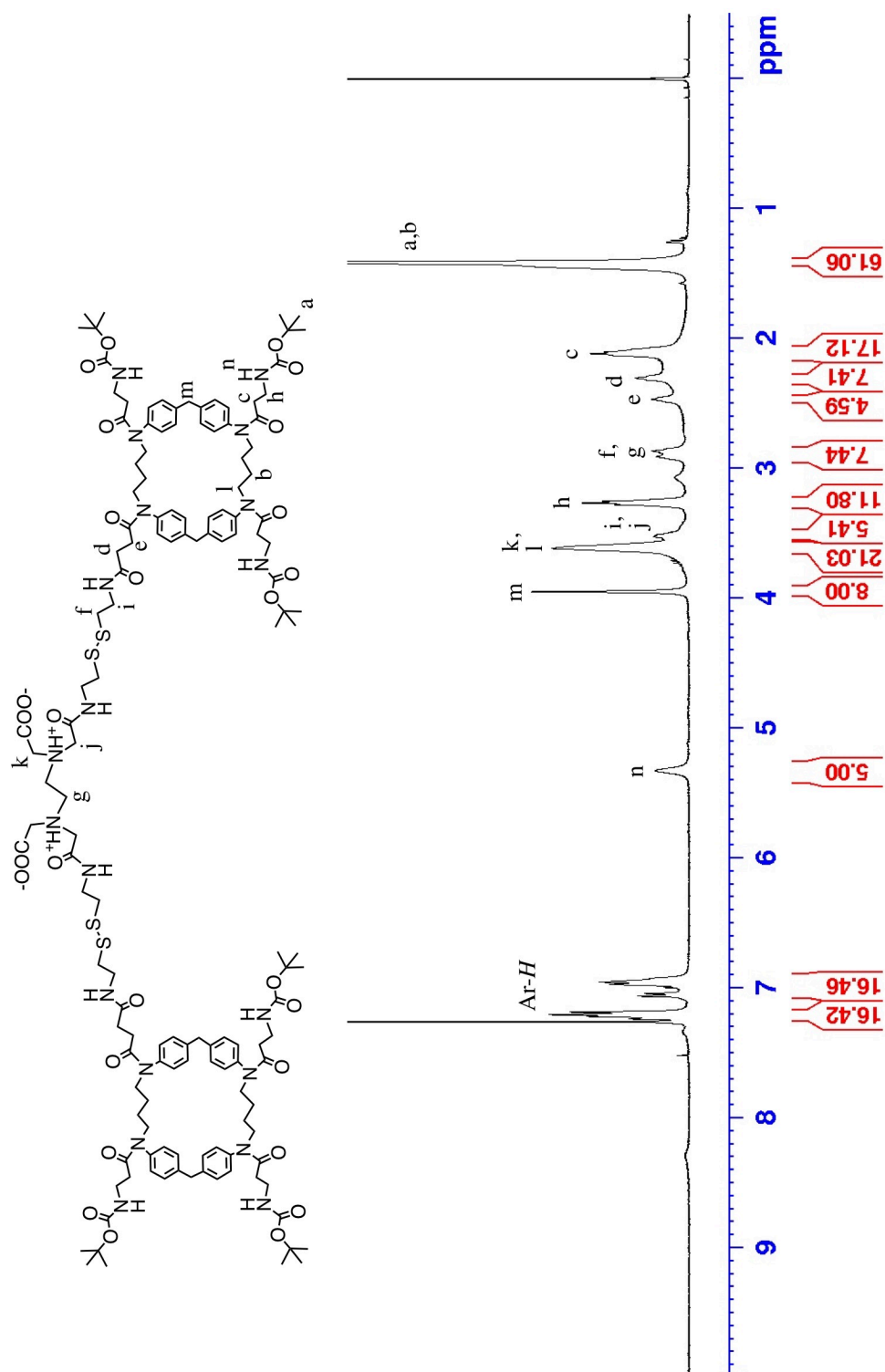


Figure S3. ^1H NMR spectrum of compound **5** (400 MHz, CDCl_3 , 298K).

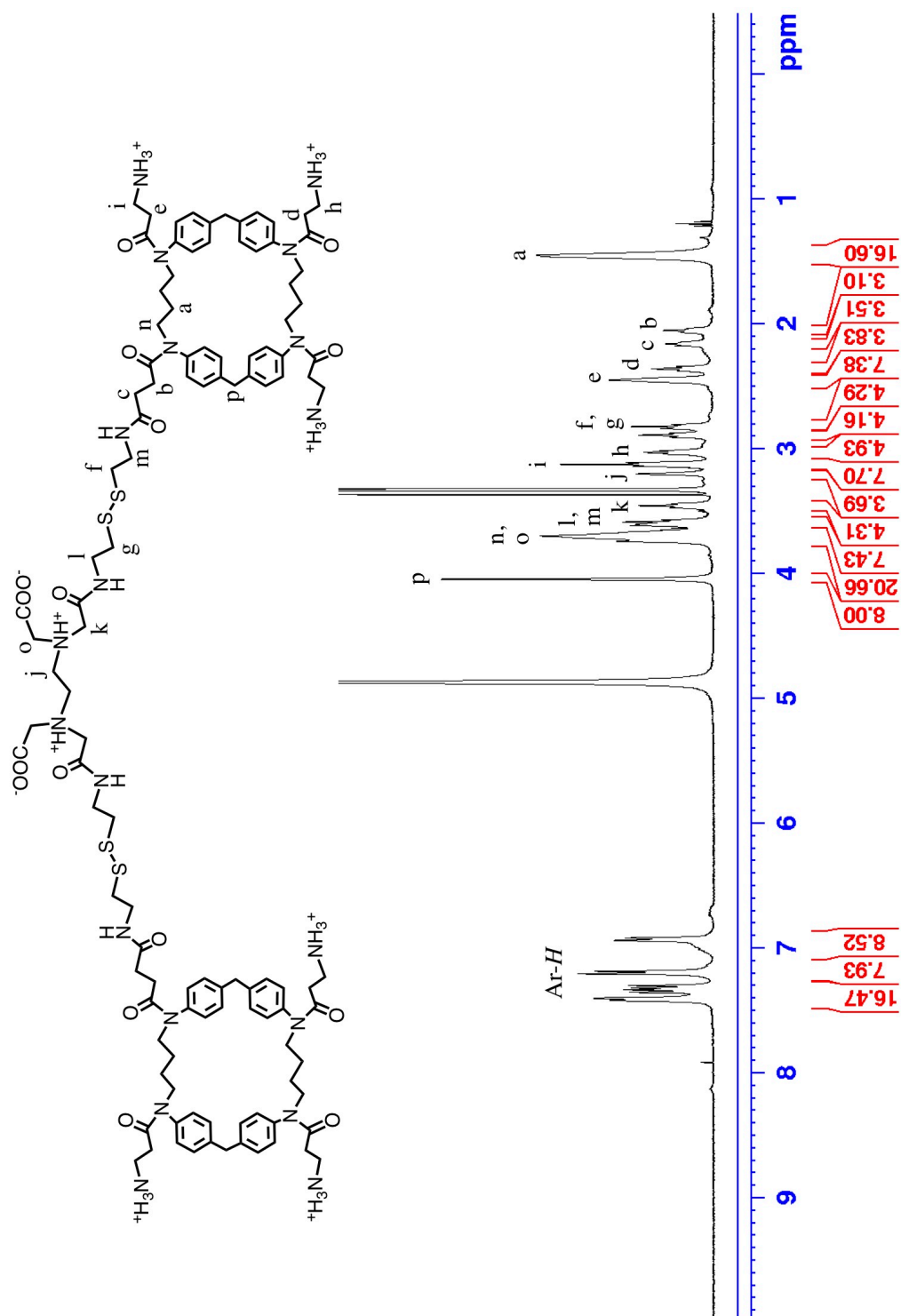


Figure S4. ^1H NMR spectrum of compound **1** (400 MHz, CD_3OD , 298K).

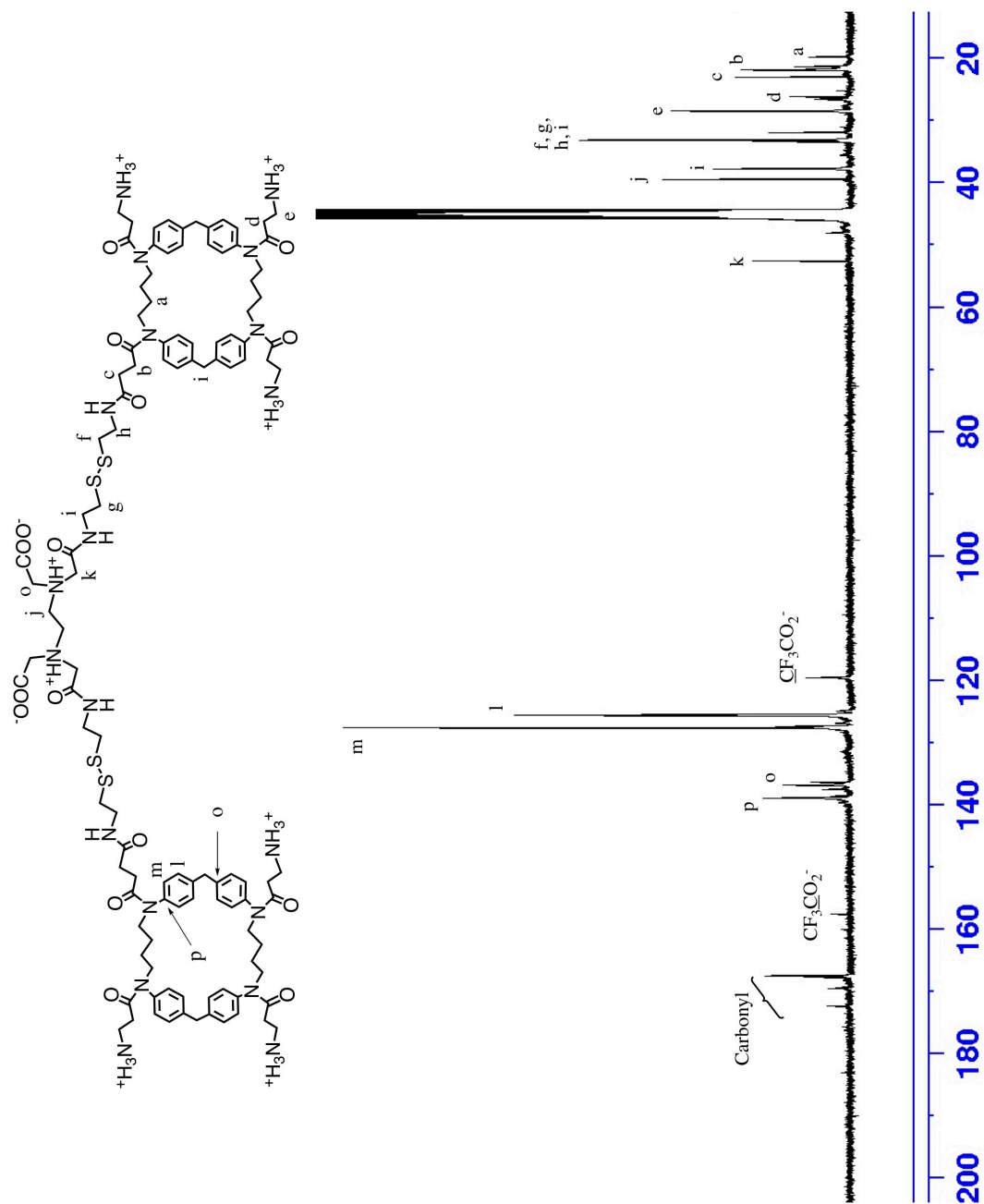


Figure S5. ^{13}C NMR spectrum of compound **1** (100 MHz, CD_3OD , 298K).

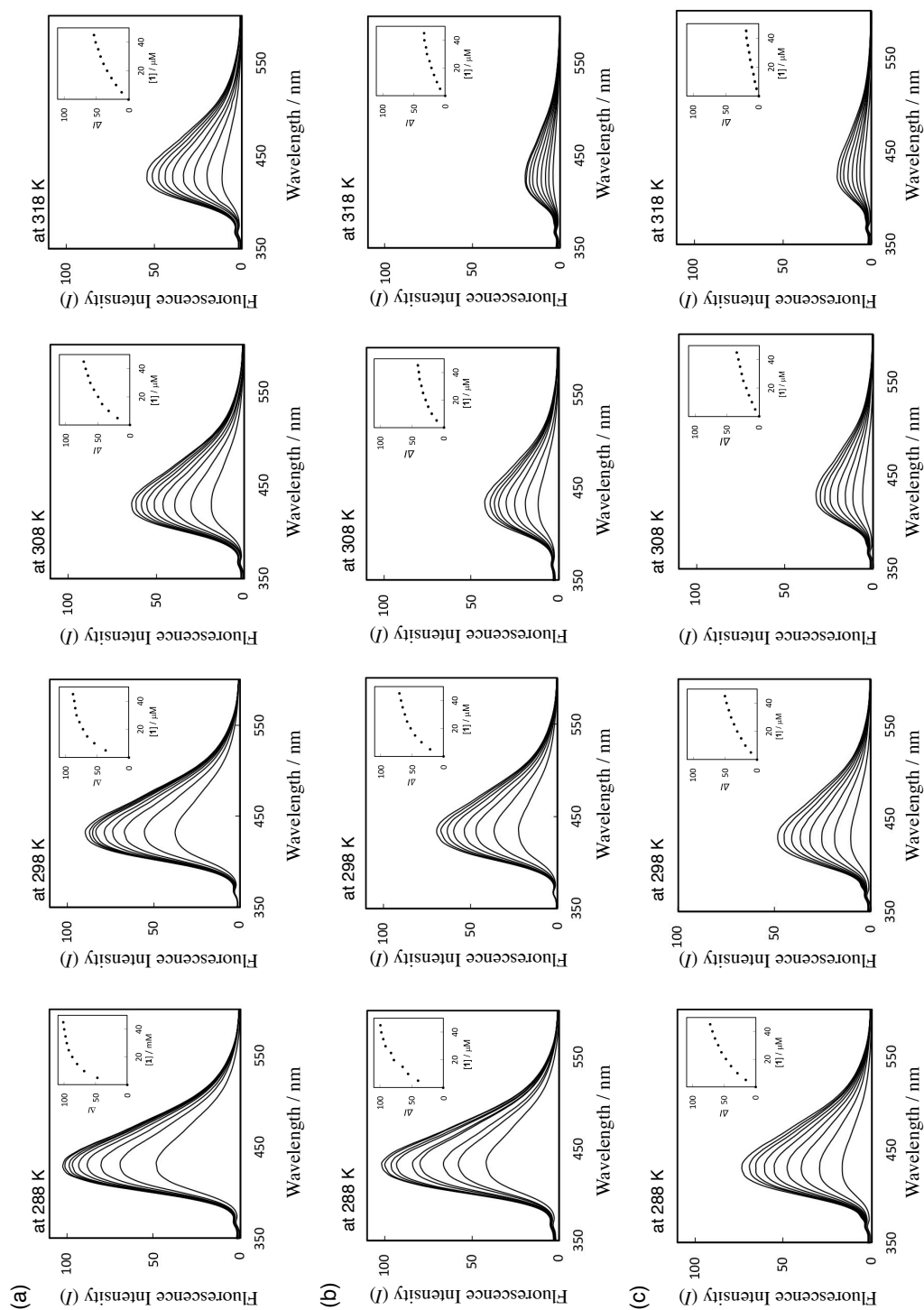


Figure S6. Fluorescence spectra for aqueous of TNS (1.0 μM) upon addition of **1** in aqueous buffer at 288, 298, 308, 318 K at pH 3.8 (a), 7.4 (b), and 10.7 (c). $[\mathbf{1}] = 0, 5, 10, 15, 20, 25, 30, 35, 40, \text{ and } 45 \mu\text{M}$. Ex. 326 nm.

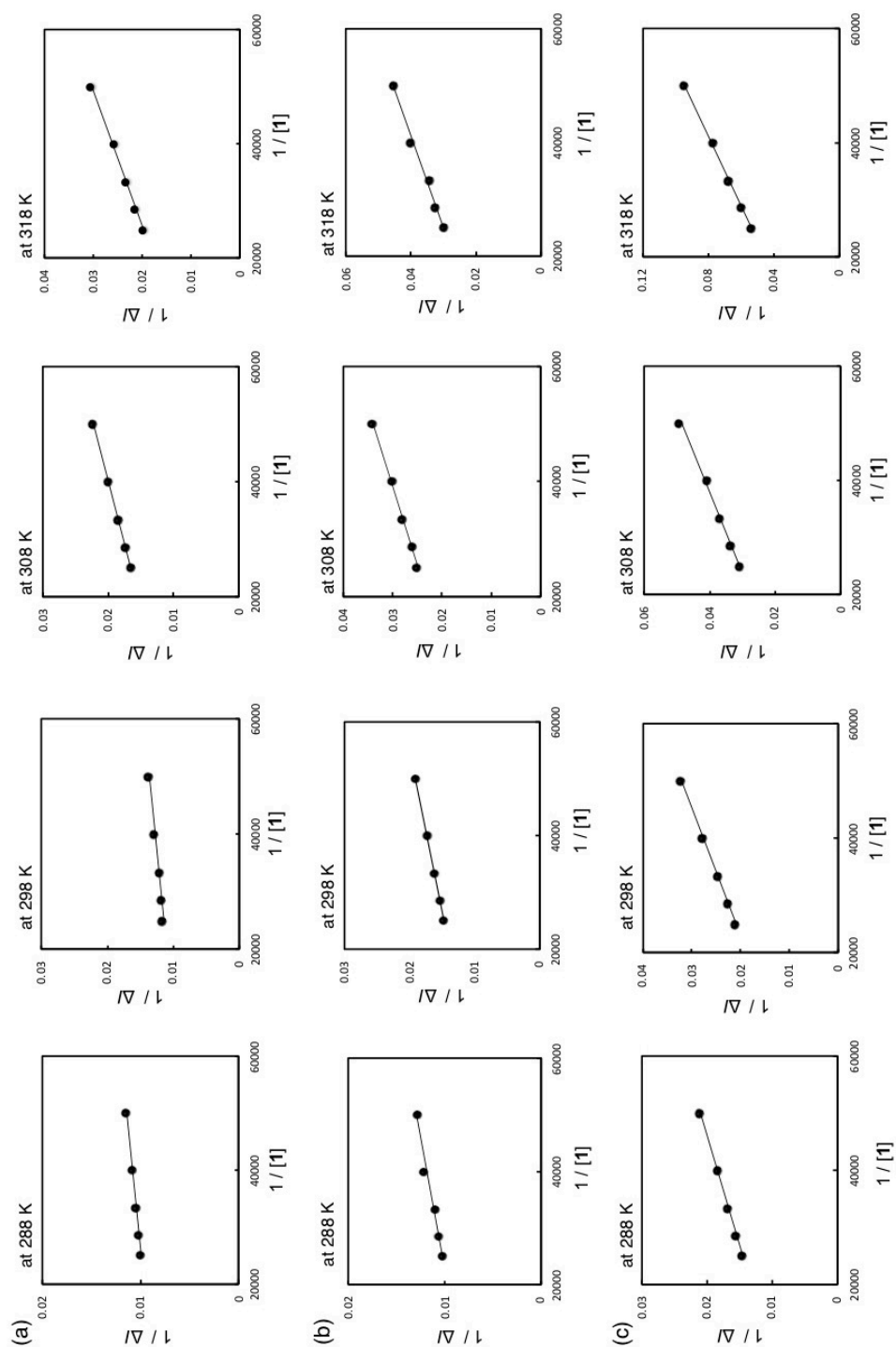


Figure S6 (continued). The corresponding double-reciprocal plots of the extent of change in fluorescence intensity against the total concentration of **1** at 288, 298, 308, 318 K at pH 3.8 (a), 7.4 (b), and 10.7 (c).

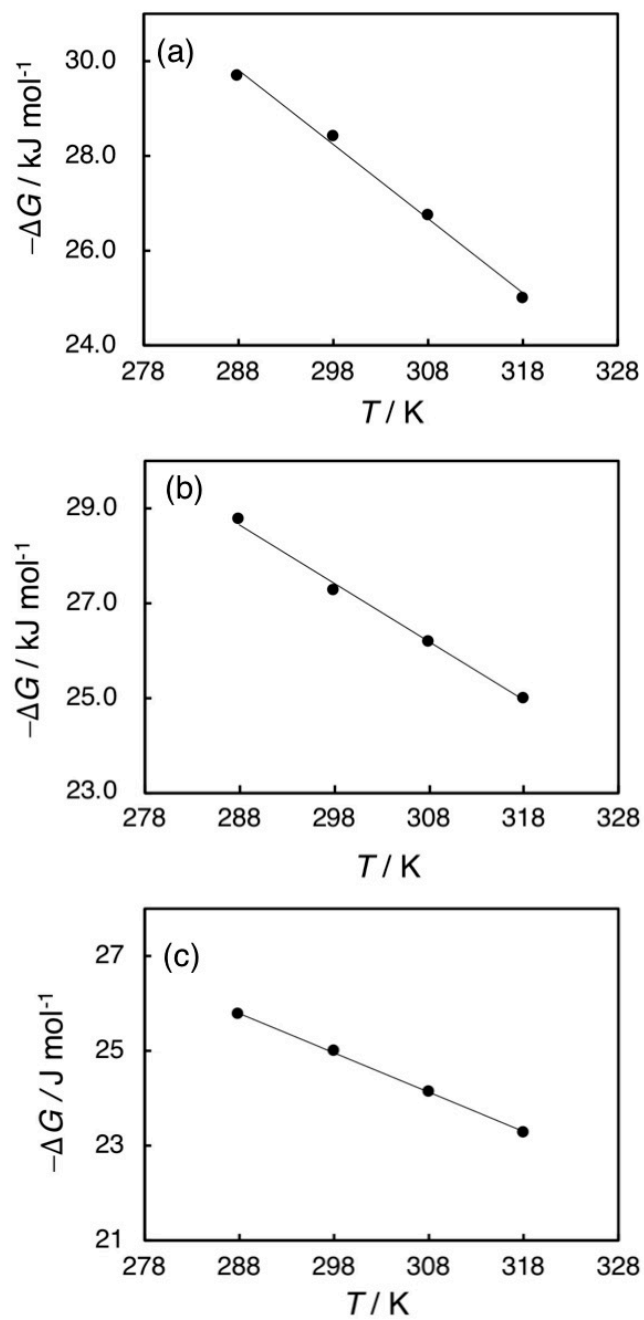
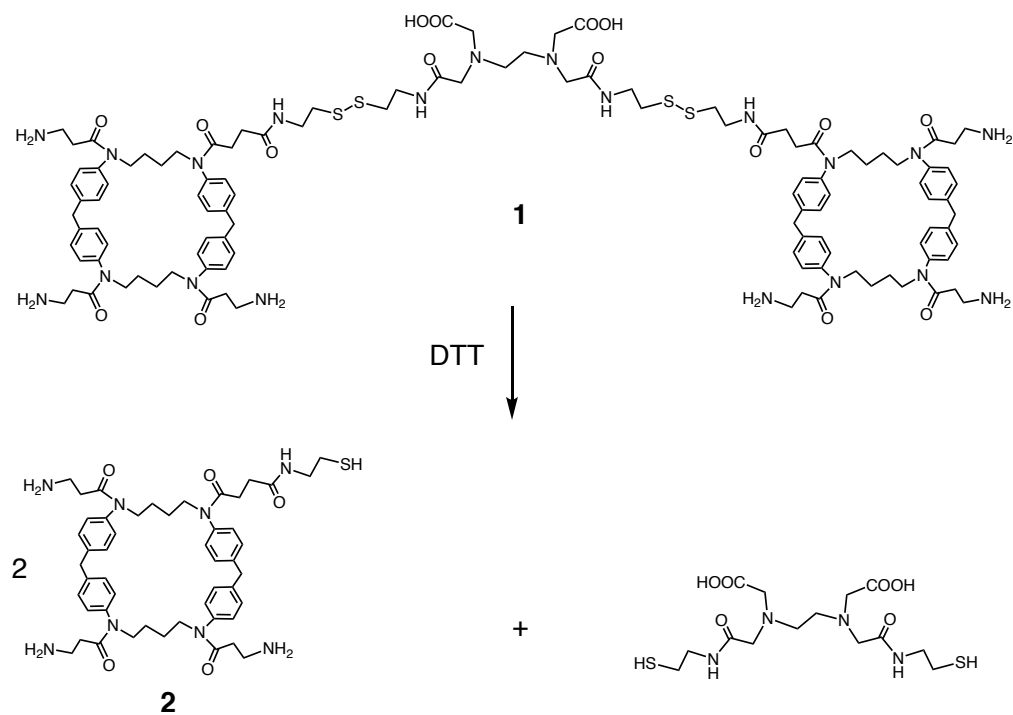


Figure S7. van't Hoff plots at pH 3.8 (a), 7.4 (b), and 10.7 (c)



Thiol derivative of cyclophane
M denotes, $C_{49}H_{64}N_8O_5S$

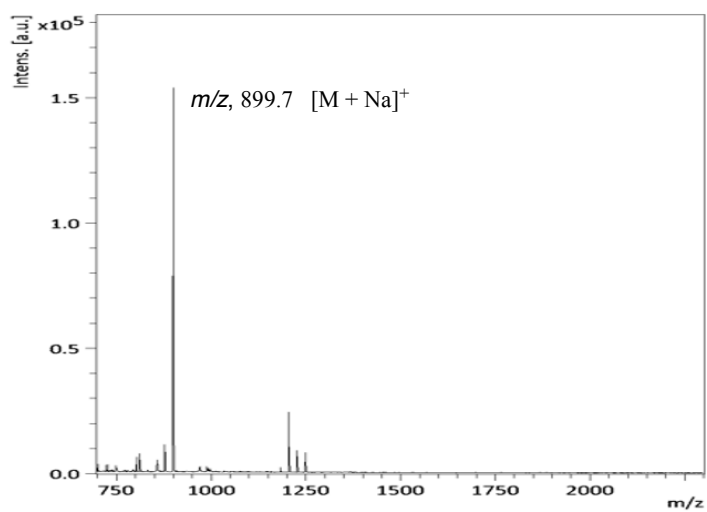


Fig. S8. MALDI-TOF MS spectra of **1** in the presence of DTT. Detection of the peaks originated from the thiol derivative of EDTA was difficult due to fragments of matrix with molecular weights less than 500 Da.

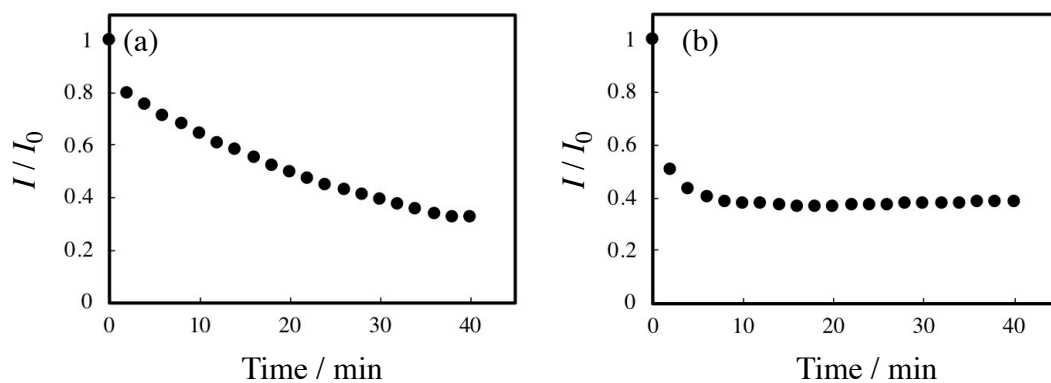


Figure 9. Time course for changes of fluorescence intensity originating TNS (1.0 μM) in the presence of **1** (25 μM) upon addition of GSH (50 μM) in aqueous buffer at pH 7.4 (a) and 10.7 (b)