

Supporting Information

Synthesis and Halochromic Behavior of Resorufin-Based Monomer, and Redox-Responsive Optical Properties of Both Monomer and Polymer

Haruto Tateki and Aohan Wang

Chemistry Course, Major in Science of Environmental Systems, Graduate School of Natural Science and Technology, Shimane University, Matsue, Shimane 690-8504, Japan

Table of Contents

1. Numbering of 2,8-dibromo-7-octyloxyresorufin	S1
2. ¹ H NMR spectrum of 2,8-dibromo-3 <i>H</i> -phenoxazin-3-one sodium salt	S1
3. Solubility test results of compound-1 and monomer.	S2
4. PL spectra of monomer and polymer.	S2
5. NaOH treatment of 2,8-dibromo-7-octyloxyresorufin	S3
6. Acid-base responsivity of the resorufin-based polymer upon the addition of acid and base	S3

1. Numbering of 2,8-dibromo-7-octyloxyresorufin

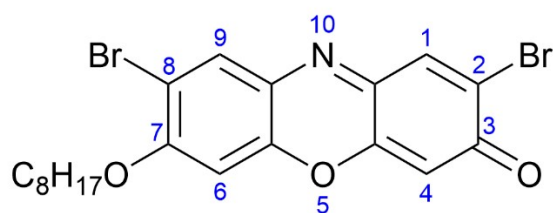


Figure S1. Numbering of the monomer, 2,8-dibromo-7-octyloxyresorufin.

2. ^1H NMR spectrum of 2,8-dibromo-3*H*-phenoxazin-3-one sodium salt

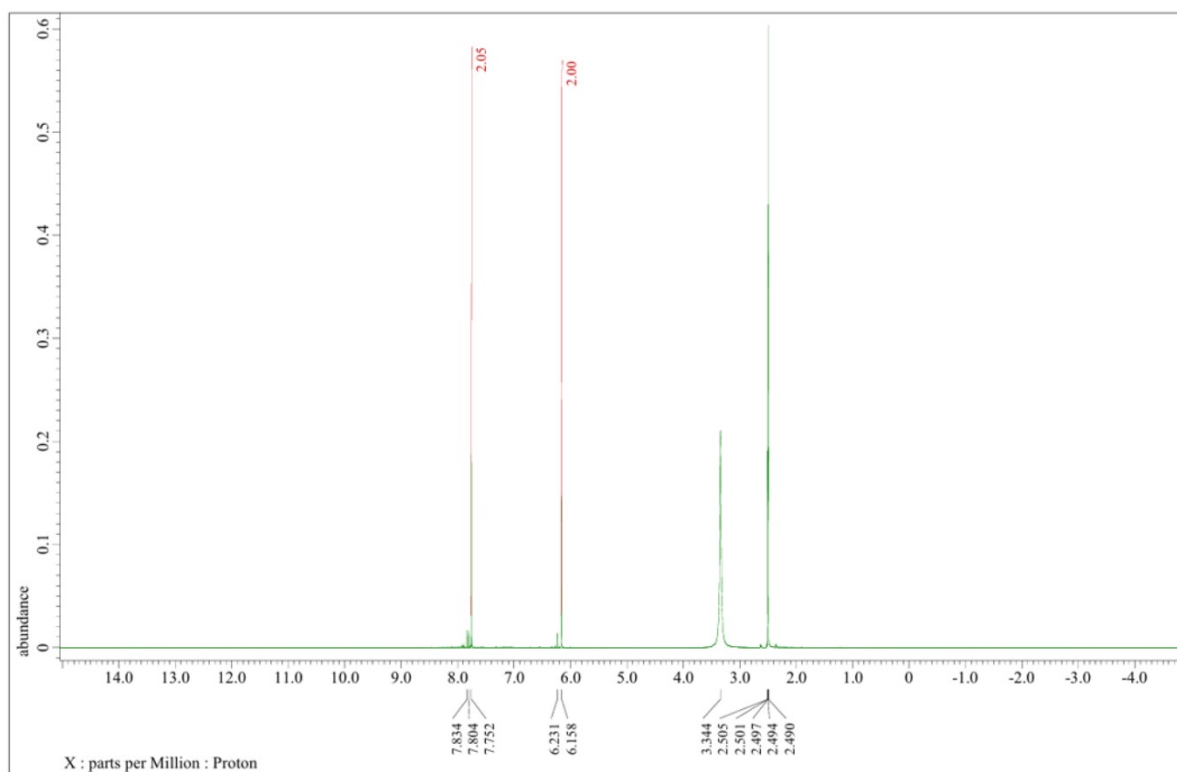


Figure S2. ^1H NMR spectrum of compound 1 ($\text{DMSO}-d_6$).

3. Solubility test results of compound-1 and monomer.

□ Table S1. Solubility of compound 1.

Solvent	r.t.	heat	Solvent	r.t.	heat
Toluene	×	×	Acetone	×	△
CH ₂ Cl ₂	×	×	MeOH	△	△
THF	×	×	EtOH	△	△
CH ₃ CN	×	×	DMF	△	○
EtOAc	×	×	DMSO	△	△
1,4-Dioxane	×	×	NMP	△	△

○ : soluble □ △ : slightly soluble □ × : insoluble

□ Table S2. Solubility of monomer.

Solvent	r.t.	heat	Solvent	r.t.	heat
Toluene	○	—	Acetone	△	△
CH ₂ Cl ₂	○	—	MeOH	△	△
THF	○	—	EtOH	△	△
CH ₃ CN	△	△	DMF	○	—
EtOAc	△	○	DMSO	△	△
1,4-Dioxane	△	△	NMP	○	—

○ : soluble □ △ : slightly soluble □ × : insoluble

4. PL spectra of monomer and polymer.

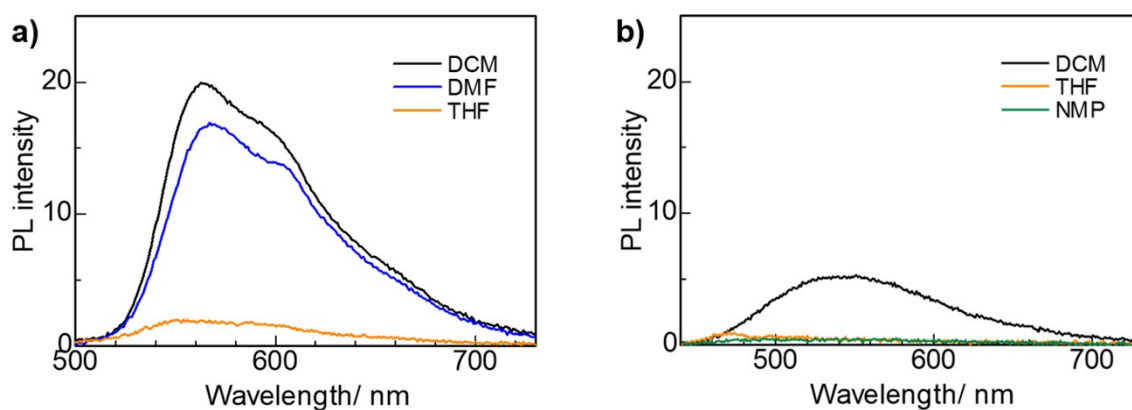


Figure S3. Enlarged PL spectra of (a) monomer and (b) polymer.

5. NaOH treatment of 2,8-dibromo-7-octyloxyresorufin

2,8-Dibromo-7-octyloxyresorufin (monomer, 0.031 g) was dissolved in a mixed THF/MeOH (THF: 100 ml, MeOH: 10 ml) solution. 1 M NaOH aq (5.5 ml) was added to the mixture and stirred for 5 min at room temperature. After the reaction, the solvent was removed under reduced pressure, and acetone was used to remove water twice. The viscous crude was crystallized with MeOH/Hexane. The precipitate was filtered and dried under vacuum for 17 h at 60 °C to afford a black solid (0.036 g). The orange color of the resorufin monomer changed to blue during the treatment of NaOHaq, as shown in Figure S4.

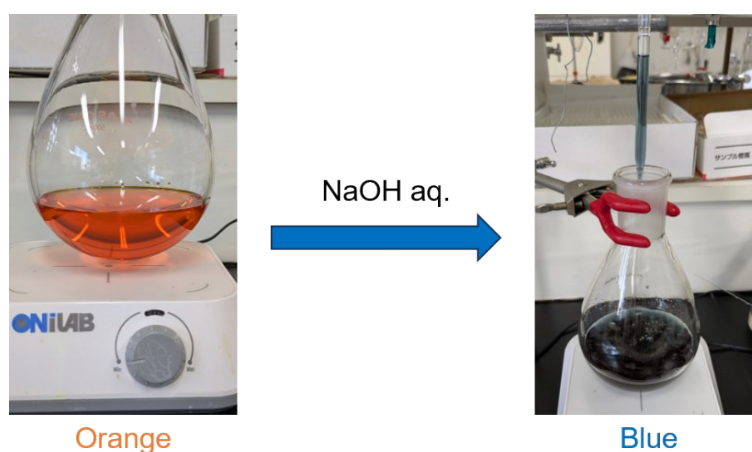


Figure S4. Color changes of the resorufin monomer during the treatment of NaOHaq.

6. Acid-base responsivity of the resorufin-based polymer upon the addition of acid and base

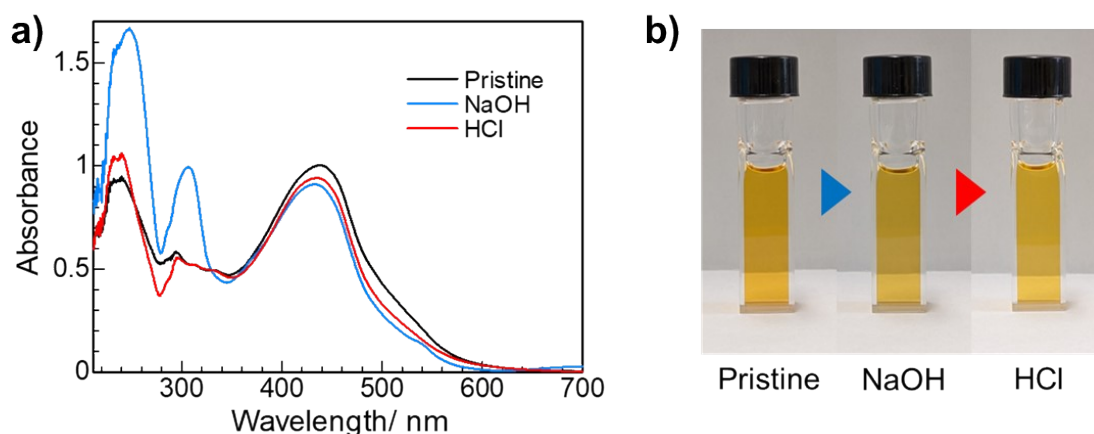


Figure S5. (c) UV-vis spectra and (d) images of resorufin-based polymer in THF/MeOH upon the addition of 0.1 M NaOHaq. and conc. HClaq.