

Temperature-controlled changeable oxygenation selectivity by singlet oxygen with a polymeric photosensitizer

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Electronic Supplementary Information (ESI†)

1. Materials

Poly(NIPAM-co-RB). NIPAM (0.61 g, 5.4 mmol), vinylbenzyl chloride (VBC, 4.7 mg, 0.031 mmol), and AIBN (19 mg, 0.12 mmol) were dissolved in toluene (5 mL). The solution was degassed by twice freeze-pump-thaw cycles. The solution was heated to 60 °C under dry N₂, kept for 18 h, and then cooled to room temperature. The resulting mixture was added slowly to diethyl ether (100 mL) with magnetic stirring. The precipitate formed was collected by centrifugation and purified by re-precipitation with MeOH (1 mL) and diethyl ether (100 mL), affording poly(NIPAM-co-VBC) as a fluffy white solid (0.58 g, 95%).^[S1] Poly(NIPAM-co-VBC) (0.28 g) and RB (0.016 g, 0.016 mmol) were dissolved in DMF (5 mL). The solution was stirred at 80 °C under dry N₂ for 16 h and then cooled to room temperature. The resultant was added slowly to diethyl ether (100 mL) with magnetic stirring. The precipitate formed was collected by centrifugation and purified by re-precipitation with MeOH (1 mL) and diethyl ether (100 mL), affording poly(NIPAM-co-RB) as a fluffy red solid (0.26 g, 94%): δ_{H} (400 MHz; CDCl₃; Me₄Si): 1.14 (s, br, 6H, -C(CH₃)₂), 1.2–2.2 (m, 3H, -CHCH₂-), 4.00 (s, br, 1H, -CH-), 6.73 (br, 1H, -NH-). The quantity of the RB unit anchored on the polymer was determined by comparison of absorbance (A_{557}) with RB ($\epsilon = 1.20 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) dissolved in MeOH at 298 K (Fig. S7). The ratio of the NIPAM (x) and RB (y) units on poly(NIPAM-co-RB) was estimated to be $x : y = 501 : 1$.

PolyNIPAM (RB free). This material was synthesized according to procedure described previously,^[S2] as follows: NIPAM (0.50 g, 4.4 mmol) and AIBN (0.014 g, 0.088 mmol) were

dissolved in toluene (5 mL). The solution was degassed by twice freeze-pump-thaw cycles. The solution was heated to 60 °C under dry N₂, kept for 15 h, and then cooled to room temperature. The resultant was added slowly to diethyl ether (100 mL) with magnetic stirring. The precipitate formed was collected by centrifugation and purified by re-precipitation with MeOH (1 mL) and diethyl ether (100 mL), affording polyNIPAM as a fluffy white solid (0.35 g, 71%): δ_{H} (400 MHz; CDCl₃; Me₄Si): 1.14 (s, br, 6H, -C(CH₃)₂), 1.2–2.2 (m, 3H, -CHCH₂-), 4.00 (s, br, 1H, -CH-), 6.73 (br, 1H, -NH-).

2. Methods

Photooxygenation. Each sensitizer was dissolved in a buffered aqueous solution (5 mL; pH 7; consisting of 0.05 M KH₂PO₄ and 0.03 M NaOH) containing **1a** and/or **2a** within a Pyrex glass tube (capacity: 20 mL). Each tube was sealed using a rubber septum cap. O₂ was bubbled through the solution for 5 min at 5 °C to avoid evaporation of the materials. The sample was photoirradiated by a high-pressure Hg lamp (100 W; Eikohsha Co. Ltd., Osaka, Japan), filtered through a Corning color filter (CS3-67) to give light wavelengths of $\lambda > 530$ nm, with magnetic stirring in a temperature range of 5–35 °C [light intensity at 530–630 nm (through the filter), 317 W m⁻²]. Substrate and product concentrations were measured by a gas chromatography (Shimadzu GC-14B, equipped with FID).

Analysis. Absorption spectra were recorded on an UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) with a 10 mm path length quartz cell.^[S3,S4] ¹H NMR spectra were obtained by JEOL JNM-AL400 (400 MHz) with Me₄Si as standard. Fluorescence and phosphorescence spectra (77 K) were measured on a Hitachi F-4500 fluorescence spectrophotometer (excitation and emission slit width: 2.5 nm), using an EtOH/diethyl ether glass (2/1 v/v) within a 4 mm cylindrical quartz tube. The singlet energy (E_{S}) and triplet energy (E_{T}) of the sensitizers were determined by procedures of literature.^[S5–7] The fluorescence quantum yield (Φ_{fl}) of the sensitizers was determined by comparison of the integrated corrected emission spectrum of standard quinine, which was excited at 366 nm in 0.1 M H₂SO₄ ($\Phi_{\text{fl}} = 0.55$).^[S8] The phosphorescence quantum yield (Φ_{phos}) was determined by a comparison of the integrated corrected emission spectrum of benzophenone in EtOH/diethyl ether glass ($\Phi_{\text{phos}} = 0.74$).^[S9] Dynamic light scattering (DLS) measurements were carried out with a laser scattering spectrometer (LB-500, HORIBA), where the light source was a 5 mW semiconductor laser ($\lambda = 650$ nm) and the scattering angle

was 90°. ^[S3,S4] Molecular weight of the polymers was determined by GPC using a JASCO HPLC system equipped with a PU-980 pump (JASCO) and a refractive index detector RI-930 (JASCO), with KF-806L column (Shodex). The oven temperature was 40 °C, and DMF containing LiBr (0.01 M) was used as the carrier solvent (flow rate: 0.6 mL min⁻¹). ^[S10]

References

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Figures

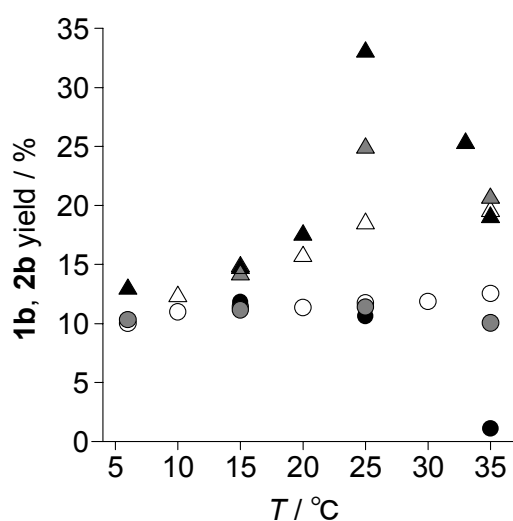


Fig. S1 Temperature-dependent changes in the yields of (circle) **1b** and (triangle) **2b**, when **1a** and **2a** (each 10 μmol) are photoirradiated separately (0.5 h) in O₂-saturated aqueous solution (pH 7). The systems are: (white) with 0.01 μmol RB, (black) with 0.58 mg poly(NIPAM-co-RB), and (grey) with 0.01 μmol RB and 0.58 mg polyNIPAM (RB-free).

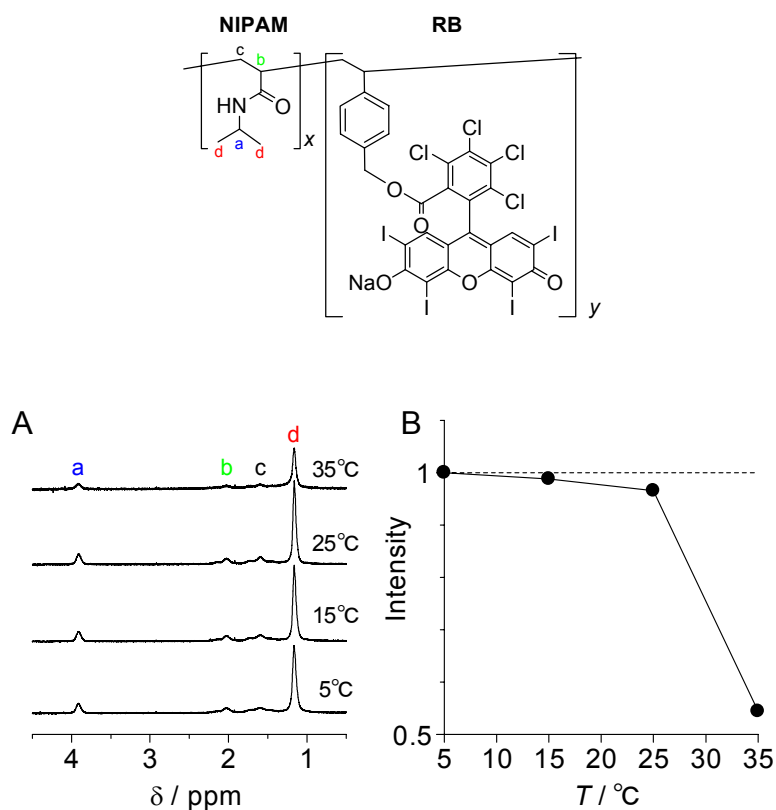


Fig. S2 (A) Change in ^1H NMR spectra of poly(NIPAM-co-RB) dissolved in D_2O (pH 7) with temperature. (B) Change in the integrated proton intensity of CH resonances of the polymer chain and NIPAM unit (a-d) as a function of temperature. The total CH intensity of poly(NIPAM-co-RB) obtained in D_2O at 5°C is set as 1.

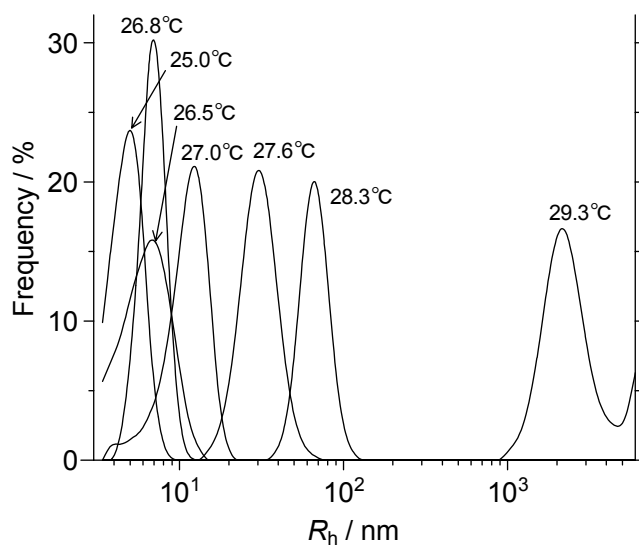


Fig. S3 Change in distribution of hydrodynamic radius (R_h) of poly(NIPAM-co-RB) in aqueous solution (pH 7) with temperature.

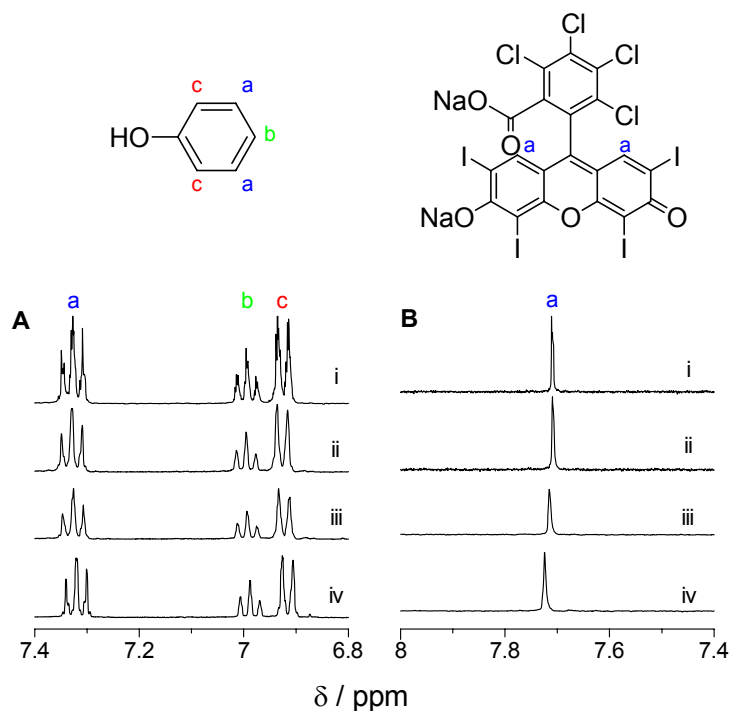


Fig. S4 (A) ^1H NMR spectra of **1a** in D_2O measured at (i) 35 °C without polymer and measured at (ii) 35, (iii) 23, and (iv) 5 °C with poly(NIPAM-*co*-RB). (B) ^1H NMR spectra of RB in D_2O measured at (i) 35 °C without polymer and measured at (ii) 30, (iii) 20, and (iv) 5 °C with RB-free polyNIPAM.

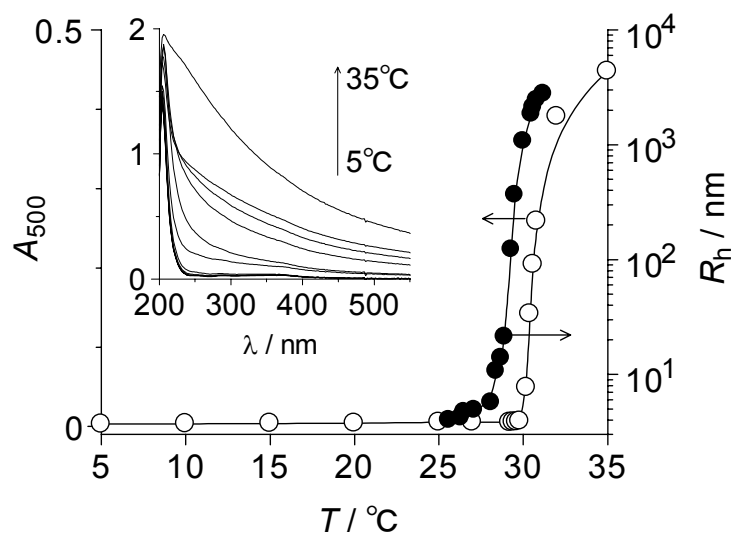


Fig. S5 Temperature-dependent change in turbidity (A_{500}) and hydrodynamic radius (R_h) of aqueous solution (pH 7) containing RB-free polyNIPAM. (Inset) Change in absorption spectra of the polymer solution. The detailed R_h data: see Fig. S6.

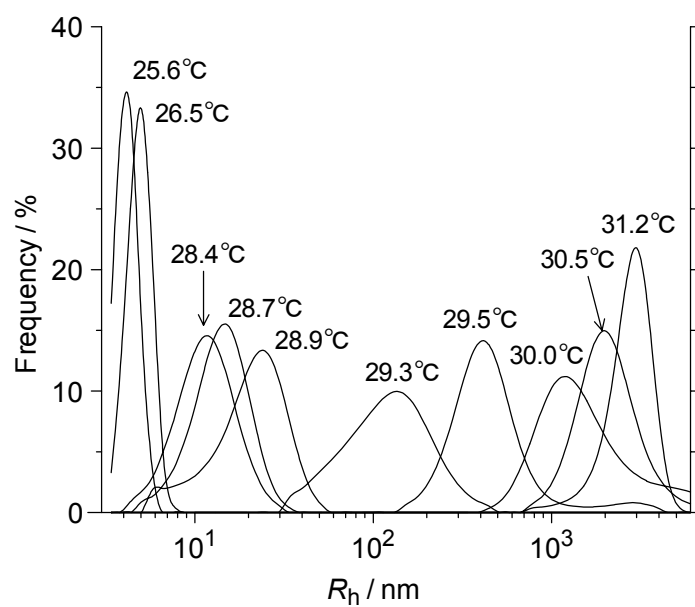


Fig. S6 Change in distribution of hydrodynamic radius (R_h) of RB-free polyNIPAM in aqueous solution (pH 7) with temperature.

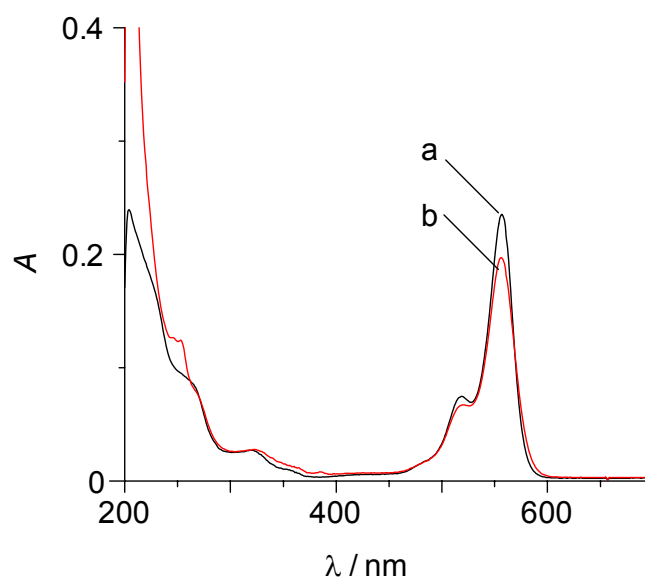


Fig. S7 Absorption spectra of (a) RB (2×10^{-6} M) and (b) poly(NIPAM-co-RB) (0.095 g/L) in MeOH at 298 K.