Supporting Information

Thermo-responsive Poly(2-isopropyl-2-oxazoline) and Tetraphenylethene Hybrids for Stimuli-responsive Photoluminescence Control

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**Experimental Section**

**Reagent and Measurement**

All of the commercially available reagents were reagent grade and used without further purification. Dichloromethane, n-hexane, and tetrahydrofuran (THF) were freshly distilled before each use. Recycling SEC was performed on a LC-9201 (JAI, Tokyo, Japan) instrument equipped with JAIGEL-1H, JAIGEL-2H, and JAIGEL-3H columns using CHCl$_3$ as the eluent. UV-vis absorption spectra were measured using a V-660 spectrophotometer (JASCO, Tokyo, Japan) equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO, Tokyo, Japan) at 25 °C. Fluorescence spectra were measured by a JASCO FP-6300 spectrophotometer equipped with a thermostatic cell holder (ETC-273T, JASCO, Tokyo, Japan) coupled with a controller (ETC-273T, JASCO, Tokyo, Japan) at 25 °C. All spectral measurements were carried out using a quartz cuvette with a path length of 1 cm. $^1$H-NMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer in CDCl$_3$. Analytical GPC was performed on a JASCO HPLC equipped with HF-403HQ and HF-404HQ columns (Shodex, Tokyo, Japan) using THF as the eluent.

**Determination of LCST**

The transmittance of the solution at 800 nm was measured using a V-660 spectrophotometer equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO). The heating rate of the sample cells was adjusted to 1.0 °C/min. The LCST points were taken as the temperature at which the transmittance reached 90% in the resulting transmittance versus temperature curves.

**Quantum Yield**

The quantum yield (QY) can be calculated from followed equation:
\[
\Phi_f^i = \frac{F_i^f s i^2}{F_s^f i s^2} \Phi_f^s
\]

where \( \Phi_f^i \) and \( \Phi_f^s \) are the photoluminescence QY of the sample and that of the standard, respectively. The subscript \( f \) is used because in most cases one is dealing with fluorescence. \( F_i^f \) and \( F_s^f \) are the integrated intensities (areas) of sample and standard spectra, respectively (in units of photons). \( f_x \) is the absorption factor (also known under the obsolete term “absorptance”), the fraction of the light impinging on the sample that is absorbed ( \( f_x = 1 - 10^{-A_x} \), where \( A \) = absorbance). As a reference compound, Tryptophan (50 \( \mu \)M) was utilized (ex:278 nm, \( \Phi = 0.12 \pm 0.01 \) in \( \text{H}_2\text{O} \)).

**Synthesis**

**General procedures of polymerization reactions:** A Schlenk flask was degassed under high vacuum and backfilled with \( \text{N}_2 \); this process was repeated three times. A solution of propargyl \( p \)-toxylate in acetonitrile was placed in the Schlenk flask, and 2-isopropyl-2-oxazoline was added. The mixture solution was stirred at 40 °C under \( \text{N}_2 \) atmosphere and monitored with analytical SEC and MALDI-TOF-MS. When the reaction was completed, the reaction mixture was cooled to room temperature and 5.0 mL of 3.0 M \( \text{NaOH} \) aqueous solution was added to the mixture. The reaction mixture was purified \textit{via} dialysis for 2 days against distilled water and then recovered by lyophilization.

**POx \(_{2500}\):** Mixture solution of propargyl \( p \)-toxylate (0.98 g, 4.66 mmol) and 2-isopropyl-2-oxazoline (11.4 g, 12.0 mL, 100 mmol) in acetonitrile (15.0 mL) was used to obtain **POx \(_{2500}\)** as white powder (8.06 g, 70 %). \(^1\)H-NMR (400 MHz, \( \text{CDCl}_3 \), 25 °C) \( \delta \) (ppm): 4.14. (m; -\( \text{CH}_2 \) on propargyl group and -C≡CH), 3.44 (broad s; -\( \text{CH}_2\)-\( \text{CH}_2 \) on the polymer backbone), 2.94-2.64 (two broad s; -\( \text{CH} \)- on the polymer side chain), 1.10 (strong broad s; -\( \text{CH}_3 \) on the
polymer side chain).

POx_{4000}: Mixture solution of propargyl p-toxylate (1.01 g, 4.82 mmol) and 2-isopropyl-2-oxazoline (19.0 g, 20.0 mL, 168 mmol) in acetonitrile (25.0 mL) was used to obtain POx_{4000} as white powder (16.0 g, 82%). \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25 °C) \(\delta\) (ppm): 4.14. (m; -CH\(_2\) on propargyl group and -C≡CH), 3.44 (broad s; -CH\(_2\)-CH\(_2\) on the polymer backbone), 2.94-2.64 (two broad s; -CH- on the polymer side chain), 1.10 (strong broad s; -CH3 on the polymer side chain).

General procedures of click reactions: To a mixture solution of TPE-N\(_3\), CuSO\(_4\)·5H\(_2\)O, and POx\(_s\) in THF (7.0 mL), aqueous sodium ascorbate solution (1.5 mL) was added. The reaction mixture was refluxed for 3 days. Then, the reaction mixture was cooled to room temperature and poured into ethyl acetate (200 mL). The organic layer was washed with water (200 mL) and brine (200 mL), and dried over anhydrous MgSO\(_4\). The organic layer was concentrated \textit{in vacuo} and purified with recycling SEC and then recovered by lyophilization to obtain TPE-POxs.

TPE-POx_{2500}: TPE-N\(_3\) (110 mg), POx_{2500} (500 mg), CuSO\(_4\)·5H\(_2\)O (250 mg), and sodium ascorbate (250 mg) were used to obtain TPE-POx_{2500} as brown powder (400 mg, 69%). \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25 °C) \(\delta\) (ppm): 7.10-6.90 (m; -CH- in phenyl ring of TPE unit), 5.42-5.37 (m; -CH\(_2\)- near phenyl ring of TPE unit), 4.65-4.52 (m; -CH- in triazole ring and –CH\(_2\)- in polymer backbone near triazole ring), 3.63 (broad s; -CH\(_2\)-CH\(_2\)- on the polymer backbone), 2.94-2.64 (two broad s; -CH- on the polymer side chain), 1.10 (strong broad s; -CH3 on the polymer side chain).

TPE-POx_{4000}: TPE-N\(_3\) (72 mg), POx_{4000} (500 mg), CuSO\(_4\)·5H\(_2\)O (250 mg), and sodium ascorbate (250 mg) were used to obtain TPE-POx_{4000} as brown powder (440 mg, 80%). \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25 °C) \(\delta\) (ppm): 7.10-6.90 (m; -CH- in phenyl ring of TPE unit), 5.42-5.37 (m; -CH\(_2\)- near phenyl ring of TPE unit), 4.65-4.52 (m; -CH- in triazole ring and –CH\(_2\)- in polymer backbone near triazole ring), 3.63 (broad s; -CH\(_2\)-CH\(_2\)- on the polymer backbone), 2.94-2.64 (two broad s; -CH- on the polymer side chain), 1.10 (strong broad s; -CH3 on the polymer side chain).
CH$_2$- in polymer backbone near triazole ring), 3.63 (broad s; -CH$_2$-CH$_2$- on the polymer backbone), 2.94-2.64 (two broad s; -CH- on the polymer side chain), 1.10 (strong broad s; -CH$_3$ on the polymer side chain).
Figure S1. Fluorescence emission change of azide-bearing TPE (50 μM) upon addition of water; a) photograph under 360 nm UV irradiation, b) fluorescence emission spectra (λ_ex = 310 nm), and c) relative fluorescence intensity at 486.5 nm.

Figure S2. Temperature-dependent transmittance changes of TPE-POx_{2500} solution (50 μM in 10 mM PBS, pH = 7.4) upon heating from 25 to 60 °C.
Figure S3. Fluorescence intensities of TPE-POx<sub>2500</sub> monitored at 475 nm upon heating from 25 to 70 °C.

Figure S4. Fluorescence emission ($\lambda_{ex} = 310$ nm) changes in TPE-Pox<sub>4000</sub> (50 μM in 10 mM PBS, pH =7.4). a) Emission spectra of TPE-Pox<sub>4000</sub> and b) TPE-Pox<sub>4000</sub> with 20 equivalent γ-CD upon heating from 25 to 70 °C.