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**Supporting Information**

# Synthesis of Photodynamic Intramolecularly Crosslinked Polyether-Copolymers In-Chain Functionalized with Hexaarylbiimidazoles

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## Experimental Section

### Materials

All chemicals were used as received unless otherwise noted.

### Synthesis of $\mathbf{2_{OTs}}$.

Into a flask, THF solution (10 mL) of $\mathbf{2_{OH}}$ (4.2 g, 2.10 mmol, 16.8 mmol for OH groups) and aqueous solution (7 mL) of NaOH (6.72 g, 168 mmol) were added. The flask was cooled in an ice bath and a THF solution (15 mL) of TsCl (6.41 g, 33.6 mmol) was slowly added. The mixture was stirred for 19.5 h at room temperature, and then water (ca. 50 mL) was added. After 1 h, the reaction mixture was poured into $H_2O$/DCM (1/1, v/v), and the DCM phase was washed with $H_2O$. The organic phase was dried over $Na_2SO_4$ and concentrated to dryness to give $\mathbf{2_{OTs}}$ as a light yellow solid. The yield was 6.09 g (91%).

### Synthesis of $\mathbf{2_{Az}}$.

Into a flask was added $\mathbf{2_{OTs}}$ (2.0 g, 0.625 mmol, 5.00 mmol for OTs groups), $NaN_3$ (975 g, 15.0 mmol), and DMF (18 mL). The mixture was stirred at 85 °C for 5 h. After cooling to room temperature, the mixture was poured into an excess amount of $H_2O$/DCM (1/1, v/v). The organic phase was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated to dryness to give light yellowish oily $\mathbf{2_{Az}}$. The yield was 1.36 g (99%).

### Synthesis of $\mathbf{2_{L}}$.

Into a flask was added $\mathbf{2_{Az}}$ (1.2 g, 0.545 mmol, 4.60 mmol for $N_3$ groups), $\mathbf{L_E}$ (2.29 g, 6.55 mmol), CuBr (313 mg, 2.18 mmol), PMDETA (456 μL, 2.18 mmol) and DMF (5

mL). The mixture was stirred at 25 °C for 3 h. After cooling to room temperature, the mixture was diluted with $CHCl_3$ and passed through a plug of alumina. The eluent was concentrated and precipitated in diethyl ether. The precipitates were dissolved in $CHCl_3$ and concentrated to dryness to give $\mathbf{2_L}$ as a light yellowish green solid. The yield was 2.6 g (95%). Number- and weight-averaged molecular weights ($M_n$ and $M_w$), peak molecular weight ($M_p$), and dispersity ($Đ = M_w/M_n$) measured by SEC calibrated with polystyrene standards; $M_n$ = 3900, $M_w$ = 4200, $M_p$ = 4200, and $Đ$ = 1.09.

**Synthesis of $\mathbf{2_H}$.**

A DCM solution (250 mL) of $\mathbf{2_L}$ (860 mg, 0.172 mmol, 1.38 mmol for lophine groups) was prepared in a flask. To this mixture, an aqueous solution (100 mL) of potassium hydroxide (1.42 g, 27.5 mmol) and potassium ferricyanide (9.06 g, 27.5 mmol) was added, and the resulting mixture was vigorously stirred in the dark. After 3 h, the DCM phase was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated to dryness to give $\mathbf{2_H}$ as a green solid. The yield was 856 mg (>99%). $M_n$, $M_w$, $M_p$, and $Đ$ measured by SEC calibrated with polystyrene standards; $M_n$ = 4300, $M_w$ = 5200, $M_p$ = 4000, and $Đ$ = 1.22.

**NMR measurements.**

$^1$H NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 500 MHz. $CDCl_3$ was used as the solvent, and chemical shifts were reported relative to tetramethylsilane (TMS) ($\delta$ = 0.00 ppm) or solvent residual signals.

**FT-IR measurements.**

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Alpha II FT-IR spectrometer in the range of 4000–400 $cm^{-1}$ with an attenuated total reflection (ATR)

module.

**SEC measurements.**

SEC measurements were performed using a Waters e-2695 high-speed liquid chromatograph equipped with RI and UV detectors. A Shodex KF-603 column (flow rate: 0.50 mL/min) was employed with THF as the eluent at 40 $^{o}$C.

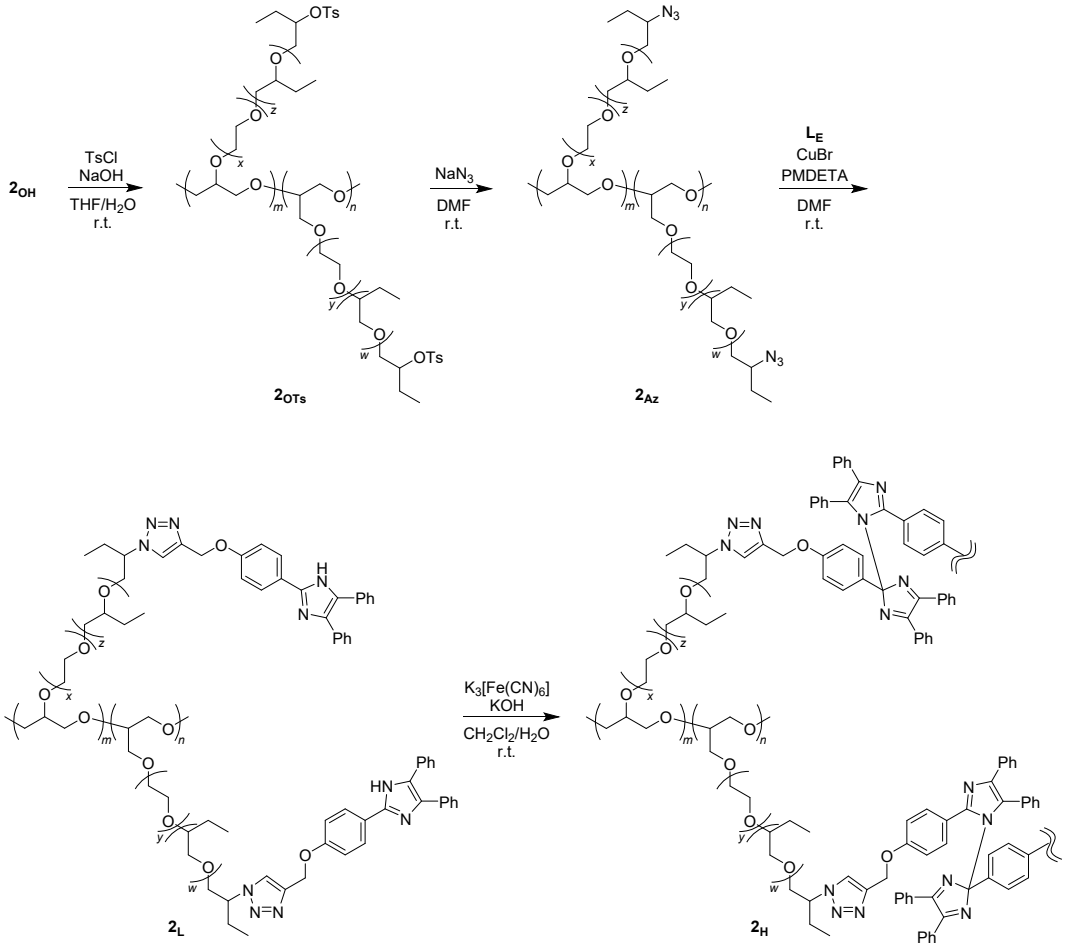
**Photoirradiation experiments.**

Photoirradiation tests were carried out using an Asahi Spectra MAX-350 xenon lamp equipped with an Asahi Spectra quartz light guide, and an Asahi Spectra LX0365 bandpass filter was used for transmitting only the wavelength of 365 nm. For demonstration, a household blue laser pointer ($\lambda \sim 405$ nm) was used.

**ESR measurements.**

ESR spectra were recorded on a JEOL JES-TE3000 spectrometer at room temperature. For photoirradiation experiments, photoirradiation was performed from a window equipped with a sample insertion opening.

**Scheme S1** Synthetic route for NPC ($\mathbf{2_H}$) from the starting PGL-based polyether-copolymer ($\mathbf{2_{OH}}$).



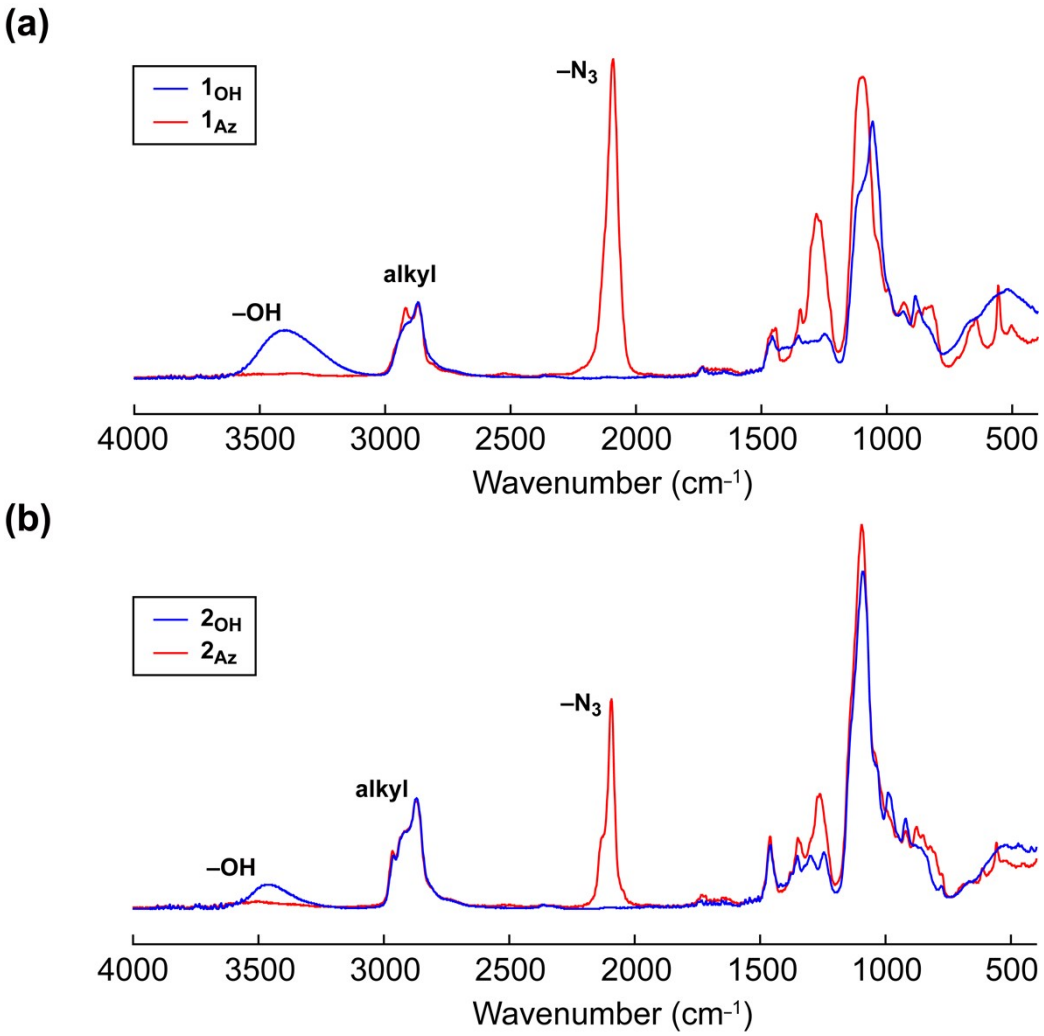



**Figure S1** FT-IR spectra of (a) $\mathbf{1}_{\mathbf{OH}}$ (blue line) and $\mathbf{1}_{\mathbf{Az}}$ (red line) and (b) $\mathbf{2}_{\mathbf{OH}}$ (blue line) and $\mathbf{2}_{\mathbf{Az}}$ (red line).

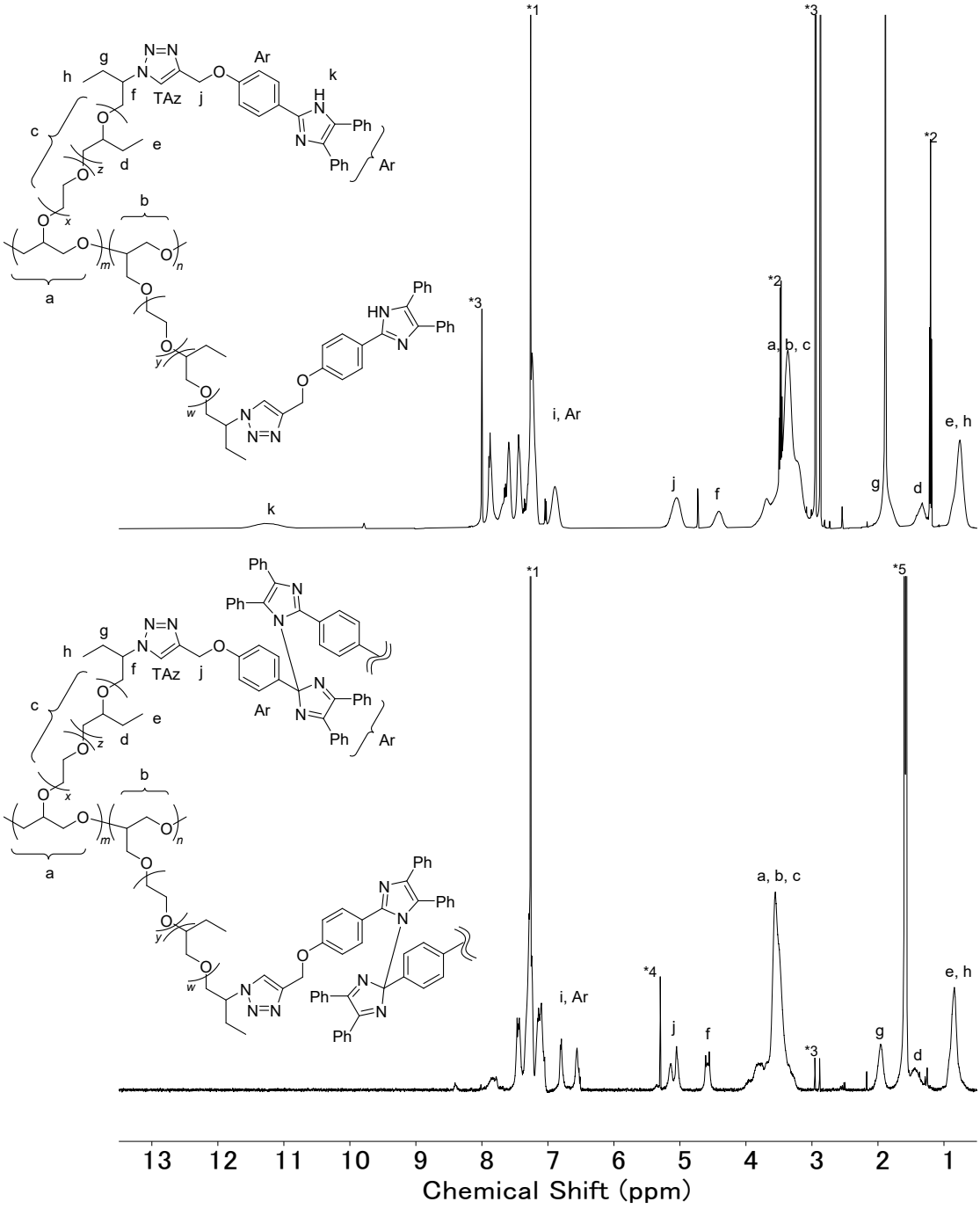



**Figure S2** $^1$H NMR spectra of $\mathbf{2_L}$ (top) and $\mathbf{2_H}$ (bottom). The signals marked with *1, *2, *3, *4, and *5 are $CHCl_3$, THF, DMF, DCM, and $H_2O$, respectively, which remained in the product due to difficulty in complete removal.

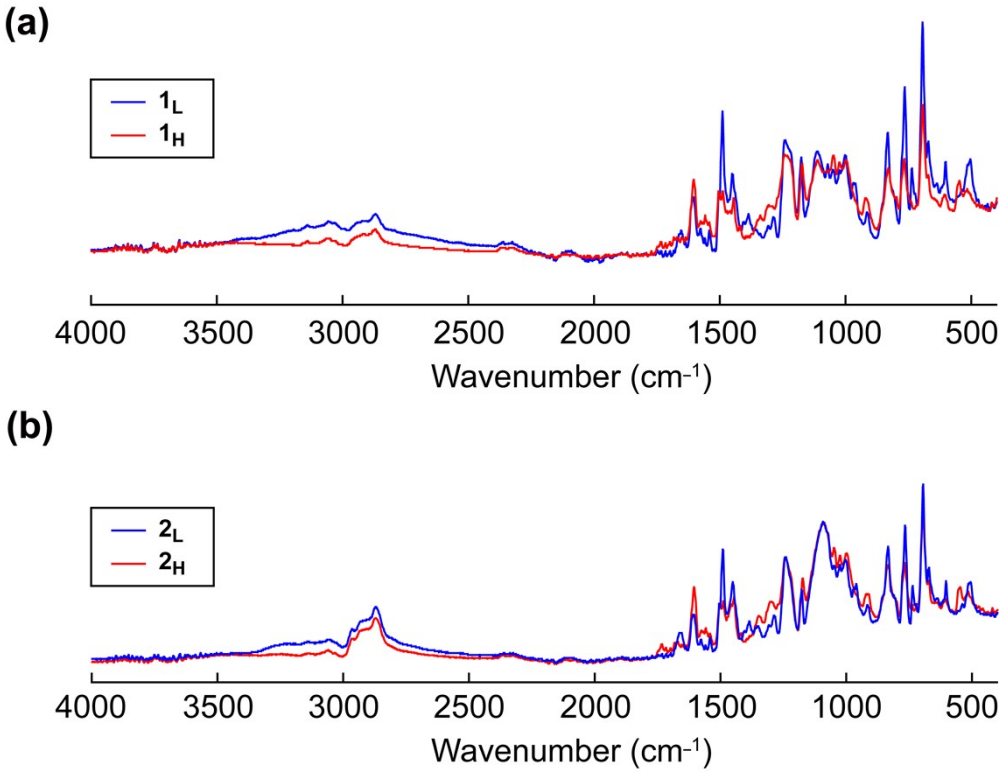



**Figure S3** FT-IR spectra of (a) $\mathbf{1_L}$ (blue line) and $\mathbf{1_H}$ (red line) and (b) $\mathbf{2_L}$ (blue line) and $\mathbf{2_H}$ (red line).

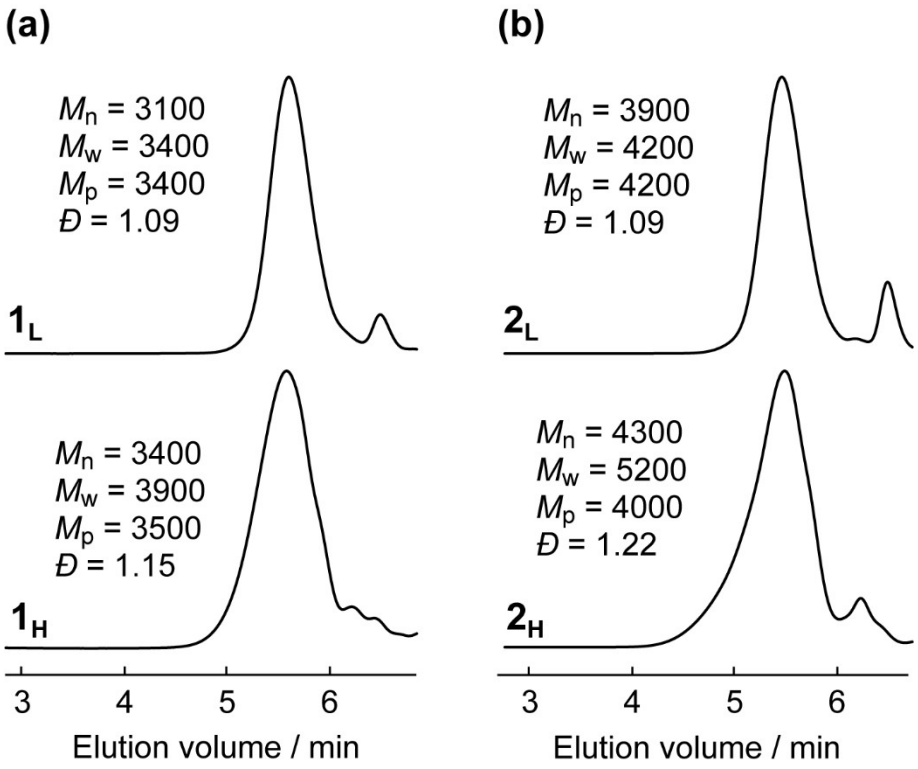



**Figure S4** SEC traces of (a) $\mathbf{1_L}$ (top) and $\mathbf{1_H}$ (bottom) and (b) $\mathbf{2_L}$ (top) and $\mathbf{2_H}$ (bottom).