SUPPORTING INFORMATION

NMR prediction of monomer.

bis(6-azidohexyl) (cyclohexane-1,3-diylbis(methylene))dicarbamate (1a) (95% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.50–1.85 (26H, m, CH_2, CH), 3.03 (4H, t, CH_2–carbamate), 3.56 (4H, t, CH_2–Cl), 4.05 (4H, t, CH_2–carbamate), 4.78 (2H, s, NH, carbamate); ^{13}C NMR ($CDCl_3$), ppm: δ 25.19, 25.23, 26.54, 28.89, 28.89, 20.42, 32.46, 34.61, (12C, CH_2), 37.95 (2C, CH), 45.00 (2C, CH_2-NH, carbamate), 47.19 (2C, CH_2-Cl), 64.68 (2C, CH_2-O, carbamate), 156.85 (2C, C=O, carbamate)

bis(6-azidohexyl) (methylenebis(cyclohexane-4,1-diyl))dicarbamate (1b) (91% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.85-2.05 (36H, m, CH_2, CH), 3.40 [Mixture of isomers] (2H, m, NH, carbamate), 3.54 (4H, t, CH_2-Cl), , 4.04 (4H, t, CH_2-O, carbamate), 4.54, 4.80 [Mixture of isomers] (2H, CH-NH, carbamate); ^{13}C NMR ($CDCl_3$), ppm: δ 25.24, 25.60, 26.53, 28.03, 28.89, 29.69, 33.44, 33.62, 33.72, [Mixture if isomers] (18C, CH, CH_2), 44.04 (1C, cyclohex-CH_2-cyclohex), 44.97 (2C, CH_2-N_3), 53.45 (2C, CH-NH, carbamate), 64.47 (2C, CH_2-O, carbamate), 155.91 (2C, C=O, carbamate)

bis(6-azidohexyl) (1,3-phenylenebis(propane-2,2-diyl))dicarbamate (1c) (98% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 1.15–1.85 (28H, m, CH_2, CH_3), 3.52 (4H, t, CH_2–Cl), 3.97 (4H, t, CH_2–carbamate), 5.07 (2H, s, NH, carbamate), 7.27 (3H, s, CH-aromatic), 7.42 (1H, s, CH-aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 26.26, 26.57, 28.95, 29.35 (8C, CH_2), 32.51 (4C, CH_3), 45.04 (2C, CH_2-Cl), 55.37 (2C, C, aliphatic), 64.25 (2C, CH_2-O, carbamate), 121.28, 123.25, 128.37 (4C, CH, aromatic), 147.20 (2C, C, aromatic) 154.87 (2C, C=O, carbamate)

bis(6-azidohexyl) (methylenebis(4,1-phenylene))dicarbamate (1d) (94% yield) ^{1}H NMR (*d*-DMSO), ppm: δ 1.31–1.77 (16H, m, CH_2), 3.63 (4H, t, CH_2–Cl), 3.86 (2H, s, Aryl-CH_2-Aryl), 4.05 (4H, t, CH_2-O, carbamate), , 7.10 (4H, d, CH-aromatic), 7.36 (4H, d, CH-aromatic), 9.51 (2H, s, CH_2-NH, carbamate); ^{13}C NMR (*d*-DMSO), ppm: δ 25.21, 26.51, 28.79, 32.43 (8C, CH_2), 40.53 (1C, Aryl-CH_2-

Aryl), 44.97 (2C, CH_2-Cl), 65.02 (2C, CH_2-O, carbamate), 118.89, 136.07 (8C, CH, aromatic), 129.38, 136.23 (4C, C, aromatic) 153.78 (2C, C=O, carbamate)

2,2-bis(bromomethyl)propane-1,3-diyl bis(hexylcarbamate) (1f) (80% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.91 (6H, t, CH_3), 1.40-1.25 (12H, m, CH_2), 1.51 (4H, quin, CH_2), 3.18 (4H, q, CH_2-NH), 3.51 (4H, s, CH_2-Br), 4.18 (4H, s, CH_2-O), 4.75 (2H, t, NH, carbamate); ^{13}C NMR ($CDCl_3$), ppm: δ 14.00 (2C, CH_3), 22.55, 26.40 (4C, CH_2), 29.83 (1C, C-CH_2), 31.45 (2C, CH_2), 34.00 (2C, CH_2-Br), 41.20, 42.80 (4C, CH_2), 63.67 (2C, CH_2-O), 155.60 (2C, C=O, carbamate)

bis(6-azidohexyl) (cyclohexane-1,3-diylbis(methylene))dicarbamate (2a) (89% yield.) ^{1}H NMR ($CDCl_3$), ppm: δ 0.50–1.90 (26H, m, CH_2, CH), 3.03 (4H, t, CH_2–carbamate), 3.27 (4H, t, CH_2–N_3), 4.06 (4H, t, CH_2–carbamate), 4.78 (2H, s, NH, carbamate); ^{13}C NMR ($CDCl_3$), ppm: δ 25.19, 25.50, 26.40, 28.75, 28.91, 30.42, 34.62 (12C, CH_2), 37.96 (2C, CH), 47.19 (2C, CH_2-NH, carbamate), 51.35 (2C, CH_2-N_3), 64.66 (2C, CH_2-O, carbamate), 154.88 (2C, C=O, carbamate)

bis(6-azidohexyl) (methylenebis(cyclohexane-4,1-diyl))dicarbamate (2b) (88% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.90-2.05 (36H, m, CH_2, CH), 3.28 (4H, t, CH_2–N_3), 3.44, 3.79 [Mixture of isomers] (2H, s, NH, carbamate), 4.05 (4H, t, CH_2–carbamate), 4.52, 4.78 [Mixture of isomers] (2H, CH-NH); ^{13}C NMR ($CDCl_3$), ppm: δ 25.49, 26.38, 28.72, 28.02, 28.90, 29.68, 32.00, 32.63, 33.42, 33.60, 33.70 [Mixture if isomers] (18C, CH, CH_2), 46.89 (1C, cyclohex-CH_2-cyclohex), 50.28 (2C, CH_2-N_3), 51.31 (2C, CH-NH, carbamate), 64.42 (2C, CH_2-O, carbamate),155.92 (2C, C=O, carbamate)

bis(6-azidohexyl) (1,3-phenylenebis(propane-2,2-diyl))dicarbamate (2c) (93% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 1.15–1.75 (28H, m, CH_2, CH_3), 3.25 (4H, t, CH_2–N_3), 3.97 (4H, t, CH_2–carbamate), 5.07 (2H, s, NH, carbamate), 7.27 (3H, s, CH-aromatic), 7.42 (1H, s, CH-aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 25.53, 26.43, 28.96, 29.34 (8C, CH_2), 28.79 (4C, CH_3), 51.40 (2C, CH_2-N_3), 55.37 (2C, C,

aliphatic), 64.24 (2C, CH_2-O, carbamate), 121.29, 123.27, 128.38 (4C, CH, aromatic), 147.21 (2C, C, aromatic) 154.88 (2C, C=O, carbamate)

bis(6-azidohexyl) (methylenebis(4,1-phenylene))dicarbamate (2d) (85% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 1.38–1.74 (16H, m, CH_2), 3.29 (4H, t, CH_2–N_3) 3.90 (2H, s, Aryl-CH_2-Aryl), 4.17 (4H, t, CH_2-O, carbamate), 6.69 (2H, s, CH_2-NH, carbamate), 7.11 (4H, d, CH-aromatic), 7.31 (4H, d, CH-aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 25.50, 26.40, 28.75, 28.80 (8C, CH_2), 40.54 (1C, Aryl-CH_2-Aryl), 51.36 (2C, CH_2-N_3), 65.01 (2C, CH_2-O, carbamate), 118.86, 135.99 (8C, CH, aromatic), 129.42, 136.29 (4C, C, aromatic) 153.74 (2C, C=O, carbamate)

2,2-bis(azidomethyl)propane-1,3-diyl bis(hexylcarbamate) (2f) (95% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.91 (6H, t, CH_3), 1.40-1.25 (12H, m, CH_2), 1.51 (4H, quin, CH_2), 3.18 (4H, q, CH_2-NH), 3.41 (4H, s, CH_2-N_3), 4.04 (4H, s, CH_2-O), 4.76 (2H, t, NH, carbamate); ^{13}C NMR ($CDCl_3$), ppm: δ 14.00 (2C, CH_3), 22.55, 26.40 (4C, CH_2), 29.83 (1C, C-CH_2), 31.45, 41.20, 43.39 (6C, CH_2), 51.64 (2C, CH_2-N_3), 63.28 (2C, CH_2-O), 155.70 (2C, C=O, carbamate)

bis(4-((8-azidooctyl)oxy)phenyl)methane (2e) (93% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 1.35–1.84 (24H, m, CH_2), 3.29 (4H, t, CH_2–N_3) 3.89 (2H, s, Aryl-CH_2-Aryl), 3.95 (4H, t, CH_2-O), 6.84 (4H, d, CH-aromatic), 7.10 (4H, d, CH-aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 26.00, 26.67, 28.84, 29.10, 29.25, 29.29 (12C, CH_2), 40.16 (1C, Aryl-CH_2-Aryl), 51.47 (2C, CH_2-N_3), 67.89 (2C, CH_2-O), 114.43, 129.71 (8C, CH, aromatic), 133.59, 157.42 (4C, C, aromatic)

1-(prop-2-yn-1-yloxy)-2,2-bis((prop-2-yn-1-yloxy)methyl)butane (3) (72% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 0.88 (3H, t, CH_3), 1.42 (2H, q, CH_2–CH_3) 2.42 (3H, t, alkyne-H), 3.40 (6H, s, CH_2), 4.11 (6H, s, CH_2-alkyne); ^{13}C NMR ($CDCl_3$), ppm: δ 7.48 (1C, CH_3), 22.71 (1C, CH_2), 42.73 (1C, C, core), 58.58 (3C, CH_2-alkyne), 70.26 (3C, CH_2), 74.05 (3C, CH, alkyne) 80.13 (3C, C, alkyne)

3-(3-(prop-2-yn-1-yloxy)-2,2-bis((prop-2-yn-1-yloxy)methyl)propoxy)prop-1-yne (4) (27% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 2.42 (4H, t, CH, alkyne), 3.55 (8H, s, CH_2), 4.15 (8H, d, CH_2-alkyne); ^{13}C NMR ($CDCl_3$), ppm: δ 44.80 (1C, C-CH_2), 58.73 (4C, CH_2-alkyne), 69.04 (4C, CH_2), 74.07 (4C, CH, alkyne), 80.04 (4C, C, alkyne)

1,3,5-tris((prop-2-yn-1-yloxy)methyl)benzene (5) (67% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 2.50 (3H, t, CH, alkyne), 4.22 (6H, s, CH_2-alkyne), 4.63 (6H, s, CH_2-aromatic) 7.33 (3H, s, CH, aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 57.32 (3C, CH_2-alkyne), 71.28 (3C, CH_2-O), 74.79 (3C, CH, alkyne), 79.54 (3C, C, alkyne), 127.17 (3C, CH, aromaric), 137.91 (3C, C, aromatic)

1,3,5-tris(prop-2-yn-1-yloxy)benzene (6) (82% yield) ^{1}H NMR ($CDCl_3$), ppm: δ 2.56 (3H, t, CH, alkyne), 4.67 (6H, s, CH_2-alkyne), 6.29 (3H, s, CH, aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 55.96 (3C, CH_2-alkyne), 77.75 (3C, CH, alkyne) 78.25 (3C, C, alkyne), 95.44 (3C, CH, aromaric), 159.34 (3C, C, aromatic)

1,3,5-tris(hex-5-yn-1-yloxy)benzene (7) (46% yield) ^{1}H NMR ($CDCl_3$), ppm: δ, 1.73 (6H, quin, CH_2), 1.91 (6H, quin, CH_2), 1.99 (3H, t, CH, alkyne), 2.29 (6H, t, CH_2-alkyne), 3.95 (6H, t, CH_2-O), 6.08 (3H, s, CH, aromatic); ^{13}C NMR ($CDCl_3$), ppm: δ 18.15 (3C, CH_2-alkyne), 25.06, 28.24 (6C, CH_2-CH_2), 67.29 (3C, CH_2-O), 68.63 (3C, CH, alkyne), 84.09 (3C, C, alkyne), 93.86 (3C, CH, aromatic), 160.83 (3C, C, aromatic)

1,1,3,3-tetramethyl-2,4-bis(prop-2-yn-1-yloxy)cyclobutane (8) (72% yield) ^{1}H NMR ($CDCl_3$), ppm: δ, 1.08, 1.12, 1.23 (12H, s, CH_3), 2.42, 2.44 (2H, t, alkyne), 3.21, 3.35 (2H, s, C-O), 4.10, 4.12 (4H, d, CH_2-alkyne); ^{13}C NMR ($CDCl_3$), ppm: δ 15.98, 23.42 (4C, CH_3-cyclobutane), 30.30 (2C, C, cyclobutane), 40.79, 42.40 (2C, CH, alkyne), 57.85, 58.10 (2C, CH_2-alkyne), 73.74, 74.02 (2C, C, alkyne), 84.26, 86.14 (2C, C-O, cyclobutane)

Table S1. Viscosity of azide monomers.

	Azides **2a**	Azides **2b**	Azides **2c**	Azides **2d**	Azides **2e**
Viscosity (Pa · s)	0.18	5.8	0.18	5.8	0.05

Table S1. Viscosity of azide monomers was monitored using a shear rate of 20 s^{-1} at 50 ℃ via rheometer.

A rheometer (ARES, TA Instruments) incorporated with a heating stage was used to measure the viscosity of the monomers in the torque ranges from $2 \cdot 10^{-6}$ to $2 \cdot 10^{-2}$ N-m, using 200 μm thickness samples placed between 20 mm diameter quartz plates.

Figure S1. Alkyne monofunctional FTIR.

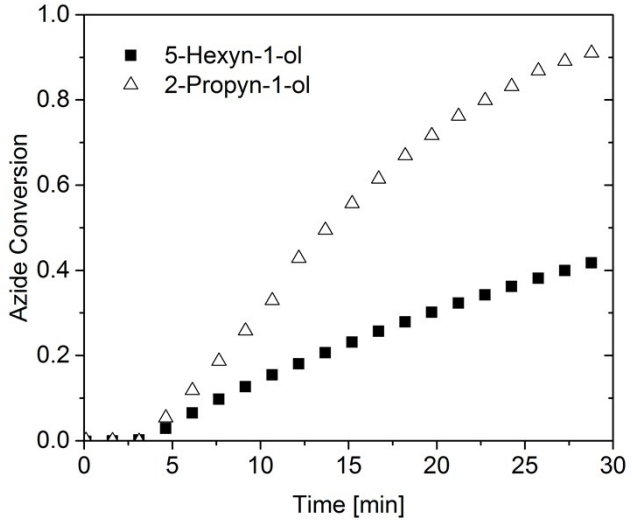

Figure S1. 2M of mono-alkynes in DMF, including 5-hexyn-1-ol and 2-propyn-1-ol, was reacted stoichiometrically with di-azides **2c** in the presence of 2 mol% $CuCl_2$[PMDETA], 4 mol% DMPA per functional group. Each mixture was irradiated for 5 minutes at ambient temperatures with 10 mW/cm^2 of 365 nm light following 3 minutes in the dark as a baseline measuring period.

Figure S2. Absorbance spectra of camphorquinone decayed over time.

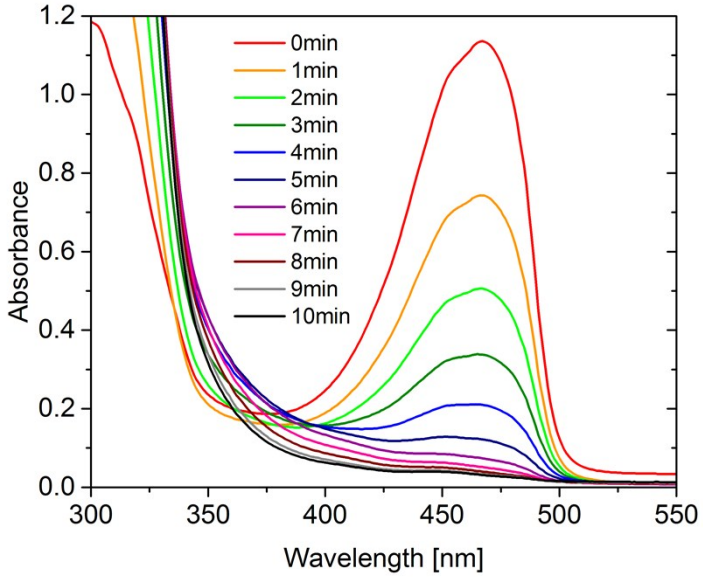

Figure **S2**. The dynamic absorbance spectra of camphorquinone during 10 minutes of continuous light exposure. A solution containing 0.044M camphorquinone and 0.044M PMDETA as a coinitiator in methanol was irradiated in a cuvett (1cm^2 area, 1.1cm thickness) at 75 mW/cm^2 using the mercury arc lamp with a 400-500nm band pass filter. UV/Vis spectra were recorded every minute of light exposure during 10 minutes of irradiation.

Figure S3. Normalized concentration of camphorquinone decayed over time.

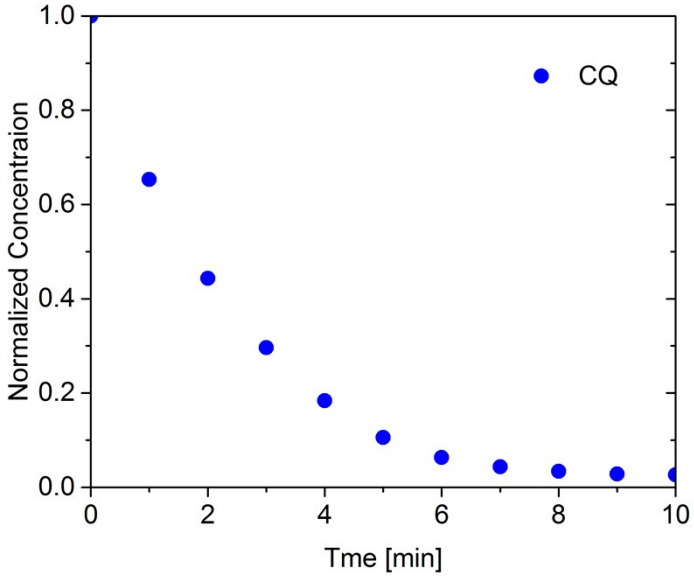

Figure **S3**. The normalized concentration of camphorquinone during 10 minutes of light exposure. A solution containing 0.044M camphorquinone and 0.044M PMDETA as a coinitiator in methanol was irradiated in a cuvett (1cm^2 area, 1.1cm thickness) at 75 mW/cm^2 using the mercury arc lamp with a 400-500nm band pass filter. UV/Vis spectra were recorded after every minute during 10 minutes of irradiation, and the absorbance of diketone chromophores at 470nm was converted to the normalized concentration of camphorquinone over time.

Figure S4. The lamp emission spectra and the molar extinction coefficient of camphorquinone.

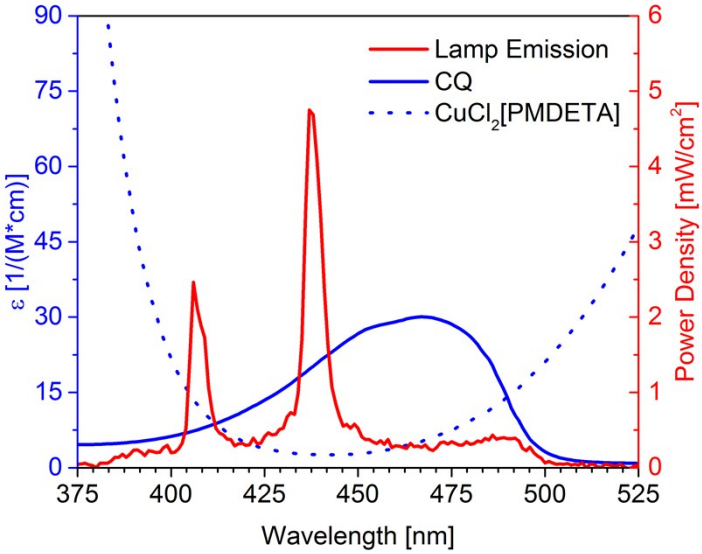

Figure **S4**. The emission spectra of the mercury arc lamp with 400-500nm band pass filter was converted to power density [mW/cm^2] at 75 mW/cm^2 of total irradiance (red line). The absorbance spectra of camphorquinone in methanol was converted to molar extinction coefficient [1/(M · cm)] (blue solid line), and the absorbance spectra of $CuCl_2$[PMDETA] in methanol was converted to molar extinction coefficient [1/(M · cm)] (blue dotted line).

A UV/Vis spectrometer was used to measure the molar extinction coefficient of CQ in the 375-525 nm wavelength range using a solution of methanol containing CQ in a cuvette with 1 cm thickness. The power density of the lamp was measured using a spectrometer as the photon counts per second and converted into units of mW/cm^2. Light exposure dose was calculated utilizing Planck's equation (

$E = N_A \cdot h \cdot \nu$) and the Beer-Lambert law ($A = \varepsilon \cdot [CQ] \cdot z = -\log\frac{I_t}{I_o}$) and written as $I_a'' = \frac{I_a' \cdot t}{[CQ]}$, where $I_a' = \frac{I_a}{N_A \cdot h \cdot \nu \cdot z}$ and $I_a = I_o - I_t = I_o(1 - 10^{-\varepsilon \cdot [CQ] \cdot z})$.