Supporting Information

Photolabile ROMP Gels Using *ortho*-Nitrobenzyl Functionalized Crosslinkers

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1. General Considerations
All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent (7.26 ppm for CHCl$_3$). All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Dry THF, dry DCM, and dry diethyl ether were obtained from an Innovative Technologies PureSolv 400 solvent purifier.

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). Electronic absorbance spectra were acquired with a Varian Cary 100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using either a PTI Quantum Master 4 equipped with a 75 W Xe lamp, or Cary Eclipse Fluorescence Spectrophotometer equipped with a Xe pulse lamp pulsed at 80 Hz, peak power equivalent to 75 kW. Rheological data was obtained on ARES G2 rheometer.

Irradiation of gels for storage modulus measurements were performed with a black-ray B-100A high intensity UV lamp (100 Watt, 365nm, power density at sample = 9 mW/cm$^2$) at fixed positions in the light path. Irradiations of gels in all other experiments were performed with a 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water filter, manual shutter, and FSQ-BG40 blue bandpass filter (Newport Corporation) at fixed positions in the light path. The power density at the sample was 25 mW/cm$^2$.

2. Materials:
5-hydroxy-2-nitrobenzyldehyde, methylmagnesium bromide solution (3.0 M in diethyl ether), N,N'-dicyclohexylcarbodiimide (DCC), chloromethyl methyl ether (MOMCl), phosphorus tribromide (PBr$_3$), sodium sulfate anhydrous, tetrabromomethane (CBr$_4$), exo-5-norbornenecarboxylic acid, 4-aminophenol, Grubbs 2$^{nd}$ generation ruthenium carbenecatalyst, potassium iodide (KI), N,N-Diisopropylethylamine (i-Pr$_2$NEt), 2-(Methylamino)ethanol, 1,4-dibromobutane and dry N,N-dimethylformamide (DMF), dry triethylamine (TEA), triphenylphosphine (PPh$_3$), methacryloyl chloride, and poly(ethylene glycol)methyl ether methacrylate (Average Mn 300) were purchased from Sigma Aldrich. 4-dimethylaminopyridine (DMAP) and sodium borohydride (NaBH$_4$) were purchased from Acros Organics. Titanium (IV) tetrachloride (TiCl$_4$) was purchased from Fluka. 4-Chloro-7-nitrobenzofurazan (NBDCl) and benzene was purchased from Alfa Aesar. Magnesium sulfate anhydrous (MgSO$_4$), sodium chloride (NaCl), hydrochloric acid (concentrated HCl), ammonium chloride (NH$_4$Cl) and potassium carbonate were purchased from Fisher Scientific. NMR solvents were purchased from Cambridge Isotope Laboratories.
3. Synthetic Procedures
CL-1, CL-2, inert CL, M1 and M3 were synthesized according to our previously published study on photoreactive ROMP gels.¹

5-hydroxy-2-nitrobenzenemethanol 1. To a 50mL three neck round bottom flask was added NaBH₄ (0.23g, 6.1 mmol) and methanol, stirred. A methanol solution of 2-nitro-5-hydroxybenzyldehyde (0.50 g, 3.0 mmol) was added dropwise into the flask at 0 °C. (Attention: the mixture may react violently due to the presence of the phenol group) The reaction mixture was then allowed to warm up to ambient temperature and stirred for 2 hours. The reaction was then poured into H₂O. The pH of the solution was adjusted to around 6 by 0.1M HCl. The solution was then extracted with diethyl ether three times, dried over MgSO₄, filtered, and concentrated using a rotary evaporator to yield 1 as a light brown solid with no further purification. Yield: 0.50 g (99%). ¹H NMR (500 MHz, MeOD): 8.09 (d, J=9 Hz, 1 H), 7.26 (dd, J=1, 1.5Hz, 1H), 6.78 (dd, J=9, 3Hz, 1H), 4.94 (s, 2 H).

5-hydroxy-α-methyl-2-nitrobenzenemethanol 2. Dry diethyl ether (100 mL) was cooled to -78 °C in a 250 mL three neck flask. TiCl₄ (4.7g, 0.25 mol) was added into the flask dropwise. The mixture was stirred at -78 °C and yielded yellow precipitation. 3M solution of MeMgBr in ether (8.3ml, 0.25mol) was added dropwise into the flask and the mixture turned to an orange color. The reaction was stirred for 30 minutes and the temperature of the mixture was allowed to slowly increase to around -30 °C. Then, 2-nitro-5-hydroxybenzyldehyde (1.7 g, 0.010 mol) was added into the flask very slowly. (Attention: the mixture may react violently due to the presence of the phenol group) The
reaction was stirred at around -30 °C for 3 hours, and then poured into water, extracted with ethyl acetate three times, dried over MgSO₄ and concentrated using a rotary evaporator to yield 2 as a yellow solid with no further purification. Yield: 1.7 g (95%). ¹H NMR (500 MHz, MeOD): 7.95 (d, J= 9 Hz, 1 H), 7.25 (d, J=3, 1 H), 6.76 (dd, J=2.5, 9 Hz, 1 H), 5.47 (q, J=6 Hz, 1 H), 1.44 (d, J=6 Hz, 3 H).

5-hydroxy-2-nitrobenzenemethyl bromide 3. To a 50 mL three neck round bottom flask was added 1 (0.26 g, 0.0015 mol) and 10 mL dry DMF. PBr₃ (1.0 g, 3.7 mmol) was added dropwise into the flask at -78 °C. The reaction was warmed to ambient temperature and stirred overnight. The reaction was poured into water, extracted by ethyl acetate three times, dried over Na₂SO₄ and concentrated using a rotary evaporator. The crude product was purified via flash chromatography using hexanes/ethyl acetate (1:1 v:v) as the eluent to afford 3 as a yellow solid. Yield: 0.24 g (67%). ¹H NMR (500MHz, CDCl₃): 8.10 (d, 9 Hz, 1 H), 7.00 (d, 2.5 Hz), 6.87 (dd, J=2.5, 9 Hz, 1 H), 5.87 (s, 1 H), 4.84 (s, 2 H).

5-hydroxy-α-methyl-2-nitrobenzenemethanol 4. A two neck flask was charged with 2 (0.33 g, 1.8 mmol), CBr₄ (1.0 g, 3.0 mol), PPh₃ (0.79 g, 3.0 mmol) and 25 mL dry THF. The reaction mixture was stirred overnight at ambient temperature. The reaction mixture was filtered, concentrated with a rotary evaporator and purified via flash chromatography using hexanes/ethyl acetate (1.5:1 v:v) as the eluent to afford 4 as a light brown solid. Yield: 0.43 g (97%). ¹H NMR (500 MHz, MeOD): 7.94 (d, 9 Hz, 1 H), 7.25(d, J=3Hz, 1 H), 6.83 (dd, J=2.5, 9 Hz, 1 H), 5.46 (q, J=6.5 Hz, 1 H), 1.43 (d, J= 6.5 Hz, 3 H).

5-methoxymethyl-2-nitrobenzenemethyl bromide 5. To a stirred mixture of 3 (1.0 g, 4.3 mmol) in 50 mL CH₂Cl₂ were added MOMCl (5 equiv) at 0 °C, then i-Pr₂NEt (3.0 equiv) was added. The reaction was stirred overnight at ambient temperature. After slow addition of saturated NH₄Cl at 0 °C, the mixture was extracted with CH₂Cl₂ 3 times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography using hexanes/ethyl acetate (2.5:1 v:v) to afford 5 as a light yellow solid. Yield: 1.0 g (84%). ¹H NMR (500MHz, CDCl₃): 8.14 (d, J=9.5 Hz, 1 H), 7.32 (d, J=3 Hz, 1 H), 7.09 (dd, J=2.5, 9 Hz, 1 H), 5.27 (s, 2 H), 5.01 (s, 2 H), 3.48-3.50 (m, 3 H)

5-methoxymethyl -α-methyl-2-nitrobenzenemethyl bromide 6. To a stirred mixture of 4 (0.43g, 1.8 mmol) in 20mL CH₂Cl₂ were added MOMCl (5 equiv) at 0 °C, then i-Pr₂NEt (3 equiv) was added. The reaction was stirred overnight at ambient temperature. After slow addition of saturated NH₄Cl at 0 °C, the mixture was extracted with DCM 3 times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography using hexanes/ethyl acetate (5:2 v:v) to afford 6 as a light yellow solid. Yield: 0.37 g (73%). ¹H NMR (500 MHz, CDCl₃): 7.97 (d, J=9 Hz, 1 H), 7.49 (d, J=2.5 Hz, 1 H), 7.05 (dd, J=2.5, 9 Hz, 1 H), 5.88 (q, J=6.5 Hz, 1 H), 5.24-5.30 (m, 2 H), 3.50 (s, 3 H), 1.88 (d, J=6.5, 3 H).
7. Exo-5-norbornenecaboxlyc (1.4 g, 0.010 mol), 4-aminophenol (1.3 g, 0.012 mol), DMAP (0.20 g, 0.0016 mol) and 100 mL dry THF were added into a 250 mL three neck round bottom flask. DCC (2.5g, 0.012 mol) in dry THF was added dropwise into the flask at 0 °C. The mixture was stirred overnight at ambient temperature. The reaction mixture was then concentrated in vacuo and redissolved in ethyl acetate, washed by HCl solution (pH around 3), brine, and water. The organic phase was dried over Na2SO4, filtered, concentrated with a rotary evaporator, and the crude product was further purified via flash chromatography using hexanes/ethyl acetate (2:1) as the eluent. Pink solid obtained was recrystallized from CH2Cl2. After filtration 7 was obtained as white crystals. Yield: 0.62 g (27%). 1H NMR (500 MHz, MeOD): 7.31 (q, J=2.5, 7 Hz, 2 H), 6.72 (q, J=2.5, 7 Hz, 2 H), 6.18-6.19 (m, 2 H), 2.95 (d, J=1.5 Hz, 1 H), 2.92 (s, 1 H), 2.25-2.29 (m, 1 H), 1.93-1.97 (m, 1 H), 1.76 (d, J=8.5 Hz, 1 H), 1.33-1.39 (m, 2 H).

8. A 25 mL three neck round bottom flask was charged with 5 (0.14 g, 0.51 mmol), 7 (0.12 g, 0.52 mmol), K2CO3 (0.14 g, 1.0 mmol), KI (0.016 g, 0.10 mmol) and 2 mL dry DMF. The reaction was stirred at 40 °C overnight, diluted with brine, and extracted with CH2Cl2 3 times. The combined organic phase was washed with water, dried over Na2SO4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography using hexanes/ethyl acetate (2:1 v:v) as the eluent to yield 8 as a yellow solid. Yield: 0.18 g (82%). 1H NMR (500 MHz, CDCl3): 8.23 (d, J=9 Hz, 1 H), 7.51 (d, J= 3 Hz, 1 H), 7.46 (q, J= 2, 7 Hz, 2 H), 7.11 (s, 1 H), 7.07 (q, J= 2.5, 9 Hz, 1 H), 6.97 (q, J=2.5, 7 Hz, 2 H), 6.15-6.19 (m, 2 H), 5.48 (s, 2 H), 5.25 (s, 2 H), 3.48 (s, 3 H), 3.05 (s, 1 H), 2.97 (s, 1 H), 2.11-2.17 (m, 1 H), 2.00-2.06 (m, 1 H), 1.78 (d, J=8.5 Hz, 1 H), 1.38-1.43 (m, 2 H).

9. A 25ml three neck round bottom flask was charged with 6 (0.11 g, 0.38 mmol), 7 (0.070 g, 0.31 mmol), K2CO3 (0.083 g, 0.60 mmol), KI (0.010 g, 0.060 mmol) and 2 mL dry DMF. The reaction was stirred at 40 °C overnight, diluted with brine, and extracted with CH2Cl2 3 times. The combined organic phase was washed with water, dried over Na2SO4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography using hexanes/ethyl acetate (2:1 v:v) as the eluent to yield 9 as a yellow solid. Yield: 0.068g (82%). 1H NMR (300 MHz, CDCl3): 8.08 (d, J=9 Hz, 1 H), 7.33 (d, J=2.7 Hz, 2 H), 7.30 (s, 1 H), 7.20 (s, 1 H), 6.99 (dd, J=2.7, 9 Hz, 1 H), 6.74 (dd, J=2.1, 6.9 Hz, 2 H), 6.12-6.16 (m, 1 H), 6.05-6.12 (m, 2H), 5.16 (s, 2H), 3.43 (s, 3H), 2.98 (s, 1 H), 2.92 (s, 1 H), 2.06-2.12 (m, 1H), 1.93-2.03 (m, 1 H), 1.73 (d, J= 8.1, 1 H), 1.67 (d, J=6.3 Hz, 3H), 1.30-1.40 (m, 2 H).

CL-3. To a stirred solution of 8 (0.77 g, 1.8 mmol) in 12 mL THF was added 2 mL concentrated HCl. The reaction was kept at ambient temperature overnight, diluted with brine, extracted with ethyl acetate 3 times, dried over Na2SO4, filtered and concentrated in vacuo. The crude product was purified via flash chromatography using hexanes/ethyl acetate (5:2 v:v) to yield PreCL-3 as a yellow solid. Yield: 0.67 g (97%). 1H NMR (500 MHz, MeOD): 8.16 (d, J=18 Hz, 1 H), 7.43-7.48 (m, 2 H), 7.22 (d, J=5, 1 H), 6.93-6.98 (m, 2 H), 6.83 (dd, J=5, 18 Hz, 1 H), 6.18-6.20 (m, 2 H), 5.45 (s, 1 H), 2.90-2.97 (m, 2 H),
2.25-2.31 (m, 1 H), 1.92-1.99 (m, 1 H), 1.76 (d, J=16, 1 H), 1.31-1.40 (m, 2 H).

**PreCL-3** (0.67 g, 1.8 mmol), 1,4-dibromobutane (0.18 g, 0.83 mmol), K₂CO₃ (0.35 g, 2.5 mmol), KI (0.020 g, 0.12 mmol) and 5 mL dry DMF were added into a 25 mL three neck round bottom flask. The reaction was stirred at 50 °C over 3 days, diluted with brine, extracted with CH₂Cl₂ 3 times. The combined organic phase was washed with water, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified via flash chromatography using CH₂Cl₂/ethyl acetate (10:1 v:v) as eluent to yield **CL-3** as a light yellow solid. Yield: 0.27 g (40%).

**1H NMR** (500 MHz, THF-d₈): 8.90 (s, 1 H), 8.19 (d, J=9 Hz, 1 H), 7.53-7.60 (m, 2 H), 7.37 (d, J=2.5, 1 H), 6.99 (dd, J=2.5, 9 Hz, 2 H), 6.89-6.93 (m, 2 H), 6.10-6.15 (m, 2 H), 5.45 (s, 2 H), 4.16 (s, 2 H), 3.57 (s, 2 H), 2.92 (s, 1 H), 2.86 (s, 1 H), 2.11-2.17 (m, 1 H), 2.00-2.06 (m, 1 H), 1.97 (s, 2 H), 1.83 (d, J=8, 1 H), 1.72 (s, 2 H), 1.20-1.30 (m, 2 H).

**13C NMR** (500 MHz, THF-d₈): 173.7, 164.5, 155.0, 141.0, 139.2, 138.5, 137.0, 135.2, 128.5, 121.4, 115.7, 114.5, 113.9, 69.2, 68.3, 48.7, 46.8, 45.9, 42.7, 31.0, 26.6. HRMS calculated for C₄₆H₄₆N₄O₁₀ (M + Na)⁺: 837.3106; found: 837.3097.

**CL-4**. To a stirred solution of **9** (0.060 g, 0.14 mmol) in 1 mL THF was added 0.17 mL concentrated HCl. The reaction was stirred under ambient temperature overnight, diluted with brine, extracted with ethyl acetate 3 times, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography using hexanes/ethyl acetate (2:1 v:v) to yield **PreCL-4** as a yellow solid. Yield: 0.056 g (96%).

**1H NMR** (500 MHz, MeOD): 8.06 (d, J=9 Hz, 1 H), 7.32-7.36 (m, 2 H), 7.09 (d, 3 Hz, 1 H), 6.78 (dd, J=3, 9 Hz, 1 H), 6.71-6.76 (m, 2 H), 6.15-6.19 (m, 2 H), 6.05 (q, J=6.5 Hz, 1 H), 2.90-2.94 (m, 2 H), 2.22-2.27 (m, 1 H), 1.89-1.95 (m, 1 H), 1.74 (s, 1 H), 1.72 (s, 1 H), 1.64 (d, J=6.5 Hz, 3 H), 1.28-1.38 (m, 2 H).

**PreCL-4** (0.056 g, 0.14 mmol), 1,4-dibromobutane (0.014 g, 0.065 mmol), K₂CO₃ (0.027 g, 0.20 mmol), KI (0.0030 mg, 0.018 mmol) and 0.8 mL dry DMF were added into a 5 mL three neck round bottom flask. The reaction was stirred at 50 °C over 3 days, diluted with brine, and extracted with CH₂Cl₂ 3 times. The combined organic phase was washed with water, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified via flash chromatography using CH₂Cl₂/hexanes/ethyl acetate (20:2:1 v:v:vw) as eluent to yield **CL-4** as a light yellow solid. Yield: 0.036 g (67%).

**1H NMR** (500 MHz, CDCl₃): 8.11 (dd, J=2, 9 Hz, 1 H), 7.27-7.33 (m, 2 H), 7.19-7.26 (m, 1 H), 7.15-7.18 (m, 1 H), 6.77-6.82 (m, 1 H), 6.69-6.75 (m, 2 H), 6.14-6.19 (m, 1 H), 6.06-6.13 (m, 2 H), 3.95-4.07 (m, 2 H), 2.98 (s, 1 H), 2.93 (s, 1 H), 2.06-2.13 (m, 1 H), 1.93-2.01 (m, 1 H), 1.92 (s, 2 H), 1.73 (d, J=8 Hz, 1 H), 1.66 (d, J= 6.5 Hz, 3 H), 1.31-1.40 (m, 2 H).

**13C NMR** (500 MHz, CDCl₃): 173.9, 163.6, 153.9, 143.0, 140.2, 138.6, 136.0, 128.0, 121.8, 115.9, 113.6, 112.5, 71.9, 68.1, 47.4, 46.4, 45.7, 41.7, 30.7, 25.6, 23.5. HRMS calculated for C₄₆H₅₁N₄O₁₀ (M+H)⁺: 843.3600; found: 843.3616.
NBD alcohol was synthesized following published methods.\textsuperscript{2}

NBD-Norbornene M2: NBD alcohol (0.16 g, 0.67 mmol), exo-5-norbornene carboxylic acid (0.10 g, 0.72 mmol), DCC (0.17 g, 0.83 mmol), DMAP (0.017 g, 0.14 mmol) were dissolved in 10 mL dry CH\textsubscript{2}Cl\textsubscript{2} in a 25 mL three neck round bottom flask. The reaction was stirred at ambient temperature overnight and then diluted with CH\textsubscript{2}Cl\textsubscript{2}, washed with water 3 times, dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated \textit{in vacuo}. The crude product was purified via flash chromatography using hexanes/ethyl acetate (3:1 v:v) as eluent, followed by recrystallization in ethanol to yield M2 as an orange solid. Yield: 0.13 g (54\%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 8.47 (d, J=9 Hz, 1 H), 6.19 (d, J=9 Hz, 1 H), 6.09-6.12 (m, 1 H), 6.01-6.04 (m, 1 H), 4.42-4.49 (m, 4 H), 3.48 (s, 3 H), 2.87 (d, J=1.5 Hz, 2 H), 2.05-2.09 (m, 1 H), 1.72-1.77 (m, 1 H), 1.34-1.38 (m, 1 H), 1.24-1.32 (m, 2 H). \textsuperscript{13}C NMR (500MHz, CDCl\textsubscript{3}): 175.9, 145.3, 144.7, 144.6, 138.2, 135.4, 135.1, 123.5, 101.7, 61.7, 54.2, 46.5, 46.3, 43.0, 41.9, 41.6, 30.3.

NBDMA: NBD alcohol (0.29 g, 0.0012 mol), freshly distilled methacryloyl chloride (0.20 g, 0.0019 mol) and dry pyridine (0.15 g, 0.0019 mol) were dissolved in 15 mL dry CH\textsubscript{2}Cl\textsubscript{2} in a 50 mL three neck round bottom flask. The reaction was stirred at ambient temperature overnight and then quenched by addition of water. The mixture was washed with CH\textsubscript{2}Cl\textsubscript{2} for 3 times, dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated \textit{in vacuo}. The crude product was purified via flash chromatography using CH\textsubscript{2}Cl\textsubscript{2} as eluent to yield NBDMA as an orange solid. Yield: 0.22 g (60\%). NMR results are in consistence with previous publications.\textsuperscript{3}

Poly(poly(ethylene glycol) methyl ether methacrylate-co-NBDMA) (PEGNBD). Poly(ethylene glycol) methyl ether methacrylate (0.50 g), NBDMA (0.025 g, 5% equiv by weight), AIBN (5.0 mg, 1% equiv by weight) and DMF (5 mL) were added into a 25 mL round bottom flask. The mixture was purged with argon for 20 min, and then warmed to 60 °C and stirred overnight. The cooled mixture was precipitated into copious hexane/ether mixture (1:1 v:v), centrifuged, and crude product was collected by decanting. The crude product was redissolved in 10 mL CH\textsubscript{2}Cl\textsubscript{2}, precipitated into hexane, and centrifuged. After decanting the remaining sticky liquid was dried in vacuum oven for 3 days to yield an orange gum-like liquid. Yield: 0.26 g (50\%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 8.45-8.65 (broad), 6.28-6.50 (broad), 4.4-4.7 (broad), 3.9-4.4 (broad). Mn 35367, Mw 60760, PDI 1.72.
General conditions for gelation.

Organogels.
A solution of Grubbs 2nd generation catalyst (2.4 mg) in 0.20 mL CH$_2$Cl$_2$ was added into a 20 mL vial charged with 0.20 mL of a DMF solution of monomers (40mg) and the crosslinker. The vial was swirled and gelation was observed in no more than 30 seconds. All gels were purified using Soxhlet extraction with CH$_2$Cl$_2$ over two days and dried in vacuum. In each irradiation experiment in which 2 mg of xerogel was used, the form factor of the gels was a thin sheet of thickness of approximately 1 mm.

Trapping of water soluble polymer into the hydrogel.
Grubbs 2nd generation catalyst (1.8 mg) was added into a 20 mL vial charged with 0.30 mL CH$_2$Cl$_2$ solution of M3 (50 mg), CL-4 (2.7 mg) and PEGNBD (1.0 mg). The vial was swirled and gelation was observed in about 20 minutes. All gels were purified using Soxhlet extraction with CH$_2$Cl$_2$ over two days and dried in vacuum.

4. Other Experimental Details

Rheological measurements.
Each set of measurements started with swelling 8.0 mg gel in benzene in a vial for at least 1 hr before measurement. All gel in the vial was transferred onto the rheometer and rheological data was measured. After one data point was obtained, all substance from the sample holder of the rheometer was collected into a quartz cuvette. Gel in the cuvette was either (1) irradiated for a certain amount of time with a blak-ray B-100A high intensity UV lamp, or (2) kept in the dark for certain amount of time in control experiments. Then all the substance in the cuvette was transferred back onto the rheometer to collect another data point. All experiments were performed at ambient temperature. Gel was immersed throughout the experiments and extra benzene was added if there was not enough benzene covering the gel.

Photodegradation experiments monitored by visual inspection or fluorescence spectroscopy.
Each set of experiments started with immersing about 2.0 mg of organogel in about 3 mL benzene in a quartz cuvette equipped with a small magnetic stir bar. The gel was swollen for at least 30 minutes, then the sample in the cuvette was irradiated by UV with the micro stir bar stirring at about 100 rpm. After a certain amount of time, the cuvette was left in the dark with no disturbance to allow the gel to settle to the bottom of the cuvette, after which emission spectra of the liquid portion of the sample was collected using excitation at 465nm. If further irradiation was needed, the cuvette containing the sample was irradiated again and another spectra was obtained following a similar procedure. Cuvettes were always located at the same position relative to the UV lamp. In control experiments, all conditions were the same other than that the samples were kept in the dark.

Photorelease of guest from the hydrogel
Each set of experiments started with immersing about 1.0 mg of hydrogel that had trapped fluorescent polymer guest in about 3 mL water in a quartz cuvette equipped with a small
magnetic stir bar. Other conditions are the same as in photodegradation experiments monitored by visual inspection or fluorescence spectroscopy.

5. Additional Figures

Figure S1. Control experiments of the dissolution of fluorescent polymer chains. (a) & (d) were obtained with Cary Eclipse Fluorescence Spectrophotometer. (b) & (c) were obtained with PTI Quantum Master 4 Fluorescence Spectrophotometer. (a) Red line: fluorescence emission of the photodegraded gel (with CL-1) solution irradiated for 450mins; blue line: fluorescence emission of the gel (with CL-1) sample in the dark after 540mins. (b) Blue curve: fluorescence emission of the gel (with CL-2) solution irradiated for 450mins; cyan curve: fluorescence emission of the gel (with CL-2) sample in the dark after 540mins. (c) Red curve: fluorescence emission of the gel (with CL-3) solution irradiated for 150mins; blue line: fluorescence emission of the gel (with CL-1) sample in the dark after 150mins. (d) Red curve: fluorescence emission of the gel (with CL-4) solution irradiated for 18mins; blue curve: fluorescence emission of the gel (with CL-4) solution in the dark for 15mins; cyan curve: fluorescence of the control gel (with inert CL) solution irradiated for 9 hrs.

![Inert CL](image)
Figure S2. Rheology experiments of unirradiated gels. Dynamic storage modulus (G’) and loss modulus (G’”) versus strain for the gels.

CL4 : catalyst (by mole)=1.3

CL4 : catalyst (by mole)=1.5
Figure S3. UV-induced release of fluorescent NBD-labeled methacrylic polymer PEGMA from hydrogel prepared with hydrophilic monomer M3 and crosslinker CL-4. According to the linear calibration curve, the final concentration of released fluorescent polymer was 0.9 mg/L.
Figure S4. Absorbance spectrum of fluorescent monomer M2.
6. NMR Spectra
$^1$H NMR spectrum of soluble fraction from organogel synthesis with CL-4

$^1$H NMR spectrum of soluble fraction from organogel synthesis with CL-2
7. References

