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Supporting Information

Dynamic, multimodal hydrogel actuators using porphyrin-based visible light photoredox catalysis in a thermoresponsive polymer network

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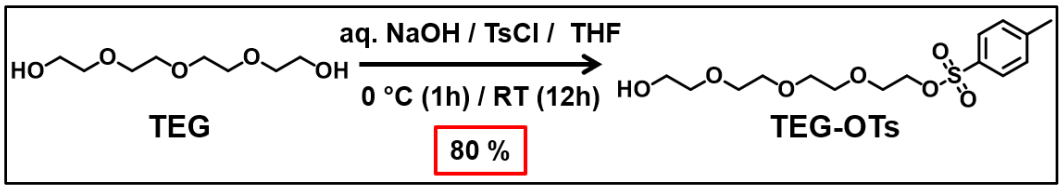
Section A. Materials / General Methods / Instrumentation

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. The photochemical reduction of polyviologens and gels was performed under an inert atmosphere of UHP N_2. All nuclear magnetic resonance (NMR) spectra were recorded on Varian Inova-500 with working frequencies of 500 (^{1}H) and 125 (^{13}C) MHz. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent: $CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm; $(CD_3)_2SO$: δ_H = 2.50 ppm and δ_C = 39.52 ppm. Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) absorbance spectra were recorded on an Agilent Cary 5000 spectrophotometer with a PbSmart NIR detector. Infrared spectroscopy (IR) was performed on a Bruker Alpha Platinum ATR FT-IR spectrometer. Size exclusion chromatography (SEC) analyses were performed on an Agilent 1260 Infinity setup with three PSS NOVEMA MAX Lux analytical 100 Å columns in tandem and 0.025 M Na_2SO_4 in H_2O mobile phase run at 23 °C. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector and the light scattering (LS) of each compound was monitored using a Wyatt Dawn Heleos-II detector. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded on Bruker Solaris 12T FT-MS, samples were prepared using 2,5 dihydroxybenzoic acid as matrix in dichloromethane or methanol. Frequency sweep (1.0 % strain, 0.1 to 30 rad s^{-1}) and strain sweep (1 rad s^{-1}, 0–50 % strain) experiments were performed on a TA AR-G2 oscillatory shear rheometer with 20 mm geometry with 0.5 N of normal force applied to gels before acquisition. For tensile testing, an MTS Systems Corp. Mechanical Testing System (MTS) Criterion 42 with a 100 N load cell was used for "dog bone" shaped samples (2.75 mm wide at their narrowest point, with a 7.5 mm gauge length) that were punched out of each hydrogel. Photochemical and bimodal reduction of the viologen-based gels using TEOA was accomplished

using two Hampton Bay desk lamp with ABI LED blue light bulbs (450 nm / 12 Watt) or with ABI LED red light bulbs (660 nm / 12 Watt). To aid in the precipitation of viologen-based compounds from their crude reaction mixtures, a Thermo Scientific Sorvall ST 8 small benchtop centrifuge was employed.

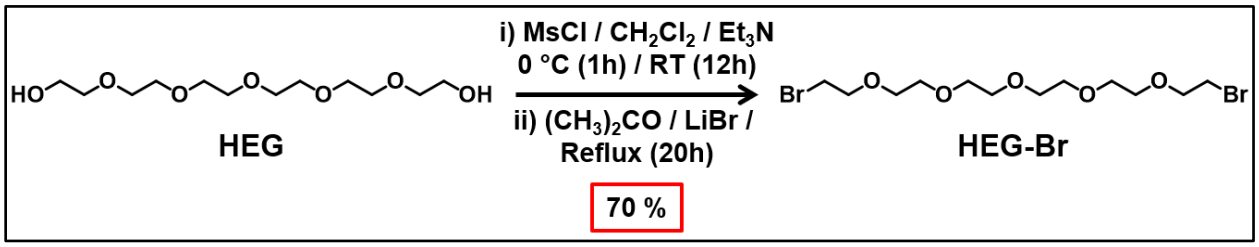
Section B. Synthetic Protocols

1) 2-(2-(2-Hydroxyethoxy)Ethoxy)Ethyl 4-Methylbenzenesulfonate (TEG−OTs)



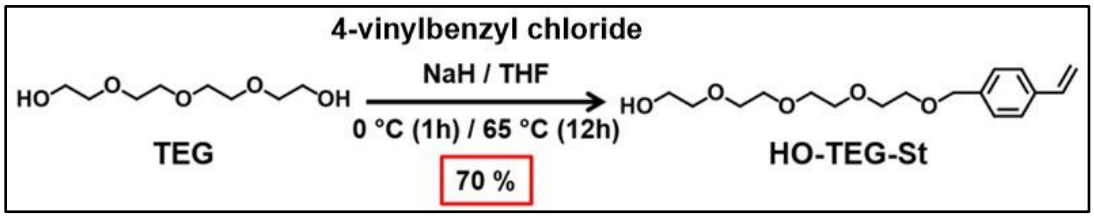
TEG-OTs was synthesized according to a previously reported literature procedure.[1] Tetraethylene glycol (TEG) (25.00 g, 128.7 mmol, 10.4 equiv) was mixed with THF (10 mL) and the solution was cooled down to 0 °C. A solution of NaOH (792 mg, 19.8 mmol, 1.60 equiv) in H_2O (5 mL) was added dropwise. A solution of *p*-toluenesulfonyl chloride (TsCl) (2.35 g, 12.3 mmol, 1.00 equiv) in THF (15 mL) was added dropwise and the mixture was stirred for 1 h at 0 °C, then warmed up to RT and stirred for 12 h. The reaction mixture was poured into ice-water (100 mL) in a separatory funnel and extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation and purified by column chromatography using EtOAc as the eluent to yield the desired product, **TEG-OTs**, as a light-yellow viscous liquid (3.4 g, 80 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.80 (d, J = 8.3 Hz, 2H); 7.34 (d, J = 8.1 Hz, 2H); 4.16 (t, J = 4.9 Hz, 2H); 3.71-3.59 (m, 14H); 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 144.94, 133.16, 129.96, 128.12, 72.61, 70.91, 70.89, 70.61, 70.48, 69.38, 68.85, 61.90, 21.78. MALDI-TOF calculated for $C_{15}H_{25}O_7S$ (*m/z*) 349.132, found: 349.187 $[M+H]^+$.

2) Dibromo-Hexaethylene Glycol (HEG-Br)



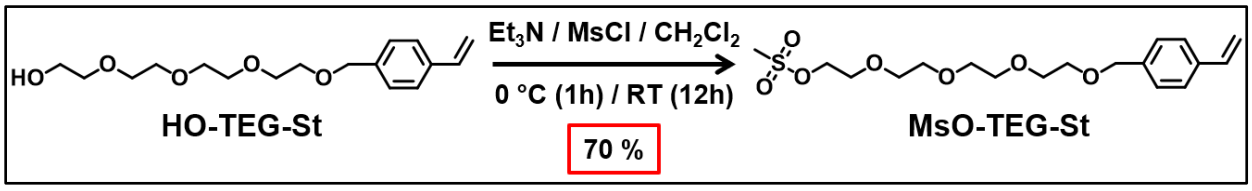
Dibromo-hexaethylene glycol (**HEG-Br**) was synthesized according to a previously reported literature procedure.[2] HEG (75.0 g, 265 mmol, 1 equiv) was dissolved in CH_2Cl_2 (300 mL) and Et_3N (67.2 g, 664 mmol, 2.5 equiv) was added. The resulting mixture was cooled to 0 °C and methanesulfonyl chloride (MsCl) (60.8 g, 531 mmol, 2 equiv) in CH_2Cl_2 (60 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 °C, then warmed up to RT and stirred for 12 h. The reaction mixture was filtered, and filtrate was washed with HCl (1 M, 1 × 150 mL), aq. $NaHCO_3$ (3 × 150 mL), brine (1 × 150 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The resulting viscous liquid was dissolved in $(CH_3)_2CO$ (350 mL), lithium bromide (LiBr) (92.2 g, 1.0 mol, 4 equiv) was added and the reaction mixture was refluxed for 20 h. The reaction mixture was cooled to RT and filtered on a pad of celite (1 cm). The filtrate was concentrated by rotary evaporation and purified by column chromatography using Hexane: EtOAc (1:1 → 0:1) as the eluent to yield the desired product, **HEG-Br**, as a light-yellow viscous liquid (75.8 g, 70 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.80 (t, J = 6.2 Hz, 4H); 3.67 (s, 16H); 3.46 (t, J = 6.4 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 71.35, 70.82, 70.74, 70.69, 30.45. MALDI-TOF calculated for $C_{12}H_{25}Br_2O_5$ (*m/z*) 407.007, found: 407.12 $[M+H]^+$.

3) Tetraethyleneglycol-Mono-4-Vinylbenzylether (HO-TEG-St)



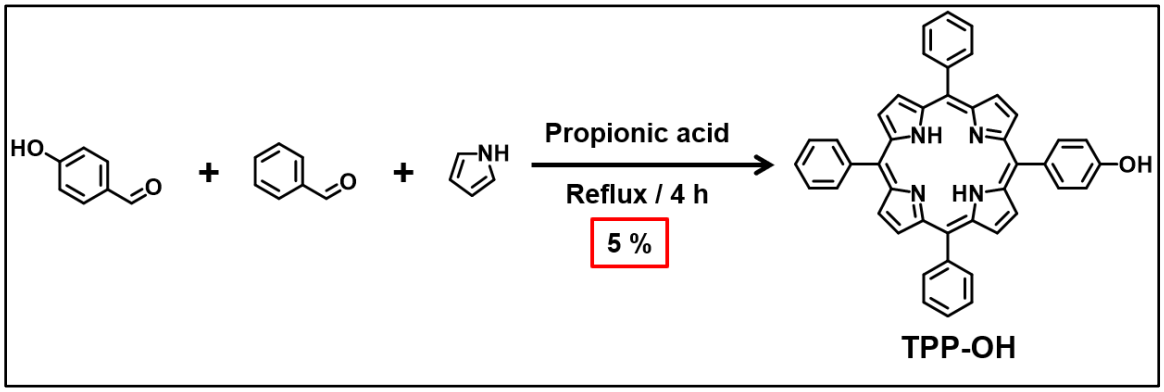
Tetraethyleneglycol-mono-4-vinylbenzylether **(HO-TEG-St)** was synthesized according to a previously reported literature procedure.[3] TEG (80.0 g, 411 mmol, 5 equiv) was dissolved in THF (70 mL), followed by the gradual addition of NaH (60 % in oil) (6.58 g, 164 mmol, 2 equiv) over 1 h at 0 °C under N_2 atmosphere. The mixture was stirred for 1 h and a solution of 4-vinylbenzyl chloride (12.57 g, 82 mmol, 1 equiv) in THF (20 mL) was added dropwise and the resulting mixture was refluxed overnight at 65 °C. The reaction mixture was quenched with H_2O (150 mL) and poured into a separatory funnel and extracted with CH_2Cl_2 (3 × 250 mL). The combined organic phases were dried over anhydrous Na_2SO_4 filtered, concentrated by rotary evaporation, and purified by column chromatography using Hexane: EtOAc (1:1 → 0:1) as the eluent to yield the desired product, **HO-TEG-St**, as a colorless viscous liquid (17.9 g, 70 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.37 (d, 2H); 7.30 (d, 2H); 6.69 (dd, 1H); 5.72 (d, J = 17.61 Hz, 1H); 5.21 (d, J = 10.9 Hz, 1H); 4.54 (s, 2H); 3.58-3.71 (m, 16H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 137.91, 137.07, 136.63, 128.07, 126.30, 113.86, 73.05, 72.64, 70.74, 70.72, 70.70, 70.68, 70.43, 69.48, 61.83. MALDI-TOF calculated for $C_{17}H_{26}NaO_5$ (m/z) 333.168, found: 333.23 $[M+Na]^+$.

4) Mesyl-Tetraethyleneglycol-4-Vinylbenzylether (MsO-TEG-St)



HO-TEG-St (17 g, 54.7 mmol, 1 equiv) was dissolved in CH_2Cl_2 (200 mL) and Et_3N (6.92 g, 68.4 mmol, 1.25 equiv) was added. The resulting mixture was cooled to 0 °C and MsCl (6.27 g, 54.7 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added dropwise and the reaction mixture was stirred for 1 h at 0 °C, then warmed up to RT and stirred for 12 h. The reaction was washed with HCl (1 M, 1 × 100 mL), aqueous $NaHCO_3$ (3 × 100 mL), brine (1 × 100 mL), extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4, followed by filtration. The solvent was removed by rotary evaporation and the resulting viscous liquid was purified by column chromatography using Hexane: EtOAc (1:1) as the eluent to yield the desired product, **MsO-TEG-St**, as a light-yellow viscous liquid (14.9 g, 70 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.38 (d, 2H); 7.30 (d, 2H); 6.70 (dd, 1H); 5.73 (d, J = 17.6 Hz, 1H); 5.21 (d, J = 10.9 Hz,1H); 4.54 (s, 2H); 4.36 (m, 2H); 3.75 (m, 2H); 3.60-3.68 (m, 12H); 3.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 137.97, 137.14, 136.66, 128.11, 126.36, 113.94, 73.11, 70.81, 70.80, 70.79, 70.75, 70.69, 69.55, 69.41, 69.16, 37.86. MALDI-TOF calculated for $C_{18}H_{28}NaO_7S$ (*m/z*) 411.145, found: 411.257 $[M+Na]^+$.

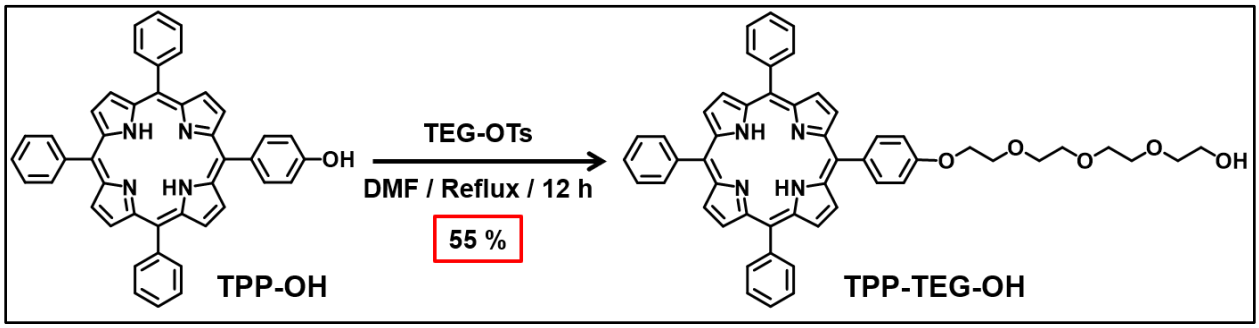
5) 5(O-Hydroxyphenyl)-10,15,20-Tri-(p-Phenyl)Porphyrin (TPP−OH)



TPP-OH was synthesized according to a previously reported literature procedure.[4] Benzaldehyde (8.60 g, 81 mmol, 3 equiv) and 4-hydroxybenzaldehyde (3.30 g, 27 mmol, 1 equiv) were dissolved in propionic acid (180 mL). This solution was heated to reflux at 140 °C for 30 min. Pyrrole (7.25

g, 108 mmol, 4 equiv) was added dropwise to the solution under N_2. The reaction mixture was refluxed for 4 h and then cooled to RT. Then, about half the volume of the reaction mixture was removed under reduced pressure and MeOH (250 mL) was added into the concentrated solution. This dark blue solution was stored overnight at 4 ˚C. After filtration, the purple precipitate was collected and washed with cold MeOH. Crude product was dried under vacuum and subsequently purified by column chromatography using Hexane: CH_2Cl_2 (1:1 → 0:1) as the eluent to yield the desired product, **TPP-OH**, as a purple solid (0.85 g, 5 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.86 (m, 8H); 8.22 (m, 6H); 8.08 (m, 2H); 7.77 (m, 9H); 7.20 (m, 2H); –2.78 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 155.54, 142.33, 142.31, 135.85, 134.87, 134.70, 127.84, 126.82, 120.23, 120.15, 113.82. MALDI-TOF calculated for $C_{44}H_{31}N_4O$ (*m/z*) 631.25, found: 631.529 $[M+H]^+$.

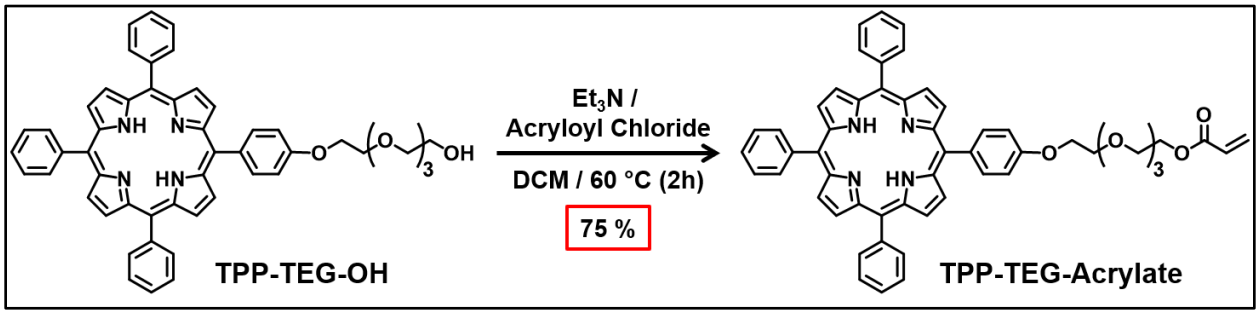
6) (4-(10,15,20-Triphenylporphyrin-5-yl)Phenoxy)Tetraethylene Glycol (TPP−TEG-OH)



TPP-OH (0.8 g, 1.2 mmol, 1 equiv), **TEG-OTs** (0.53 g, 1.5 mmol, 1.2 equiv) and K_2CO_3 (1.7 g, 12.6 mmol, 10 equiv) in 15 mL dry DMF at 80 °C under N_2 for 12 h. The mixture was then filtered, and the solvent was removed by rotary evaporation to give a purple residue, which was dissolved in $CHCl_3$ (50 mL) and washed with brine (3 × 50 mL) and then H_2O (2 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated by rotary evaporation and purified by column chromatography using EtOAc as the eluent to yield the desired product,

TPP-TEG-OH, as a purple solid (0.6 g, 55 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.86 (m, 8H); 8.22 (m, 6H); 8.12 (m, 2H); 7.77 (m, 9H); 7.30 (m, 2H); 4.43 (m, 2H); 4.06 (m, 2H); 3.79 (m, 12H); –2.76 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 158.75, 142.35,142.33, 135.71, 134.89, 134.70, 127.83, 126.81, 120.22, 120.11, 113.00, 72.72, 71.09, 70.89, 70.85, 70.55, 70.09, 67.85, 61.97. MALDI-TOF calculated for $C_{52}H_{47}N_4O_5$ (*m/z*) 807.355, found: 807.981 $[M+H]^+$.

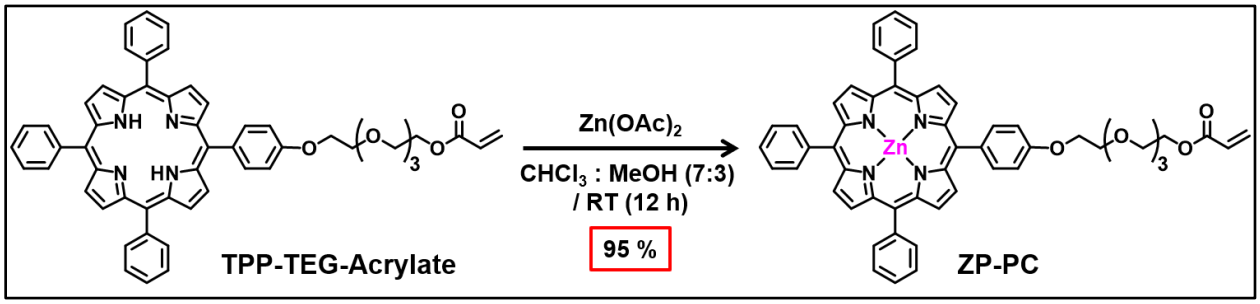
7) (4-(10,15,20-Triphenylporphyrin-5-yl)Phenoxy)Tetraethylene Glycol Acrylate (TPP−TEG-Acrylate)



TPP-TEG-Acrylate was synthesized according to a previously reported literature procedure.[5] **TPP-TEG-OH** (0.55 g, 0.68 mmol, 1 equiv), and Et_3N (0.17 g, 1.7 mmol, 2.5 equiv) were taken in dry CH_2Cl_2 (20 mL) under N_2 environment. The solution was heated to 60 ˚C and acryloyl chloride (0.123 g, 1.3 mmol, 2 equiv) in CH_2Cl_2 (5 mL) was added dropwise over a 15-min period. The reaction mixture was stirred at 60 ˚C for 2 h and then cooled to RT and diluted with $CHCl_3$ (50 mL) and followed by washing with saturated $NaHCO_3$ (3 × 50 mL) and H_2O (1 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated by rotary evaporation and purified by column chromatography using CH_2Cl_2: EtOAc (9:1) as the eluent to yield the desired product, **TPP-TEG-Acrylate**, as a purple solid (0.44 g, 75 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.86 (m, 8H); 8.22 (m, 6H); 8.12 (m, 2H); 7.77 (m, 9H); 7.30 (m, 2H); 7.30 (m, 2H); 6.44 (dd, J_1 = 1.4 Hz, J_2 = 17.3 Hz, 1H); 6.17 (dd, J_1 = 10.4 Hz, J_2 = 17.3 Hz, 1H);); 5.83

(dd, J_1 = 1.4 Hz, J_2 = 10.4 Hz, 1H); 4.42 (m, 2H); 4.36 (m, 2H); 4.05 (m, 2H); 3.88-3.75 (m, 10H); –2.75 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.23, 158.72, 142.32, 142.29, 135.63, 134.76, 134.66, 131.07, 128.42, 127.80, 126.79, 120.26, 120.20, 120.15, 112.92, 70.97, 70.82, 70.75, 69.90, 69.23, 67.67, 63.81. MALDI-TOF calculated for $C_{55}H_{49}N_4O_6$ (*m/z*) 861.365, found: 861.858 $[M+H]^+$.

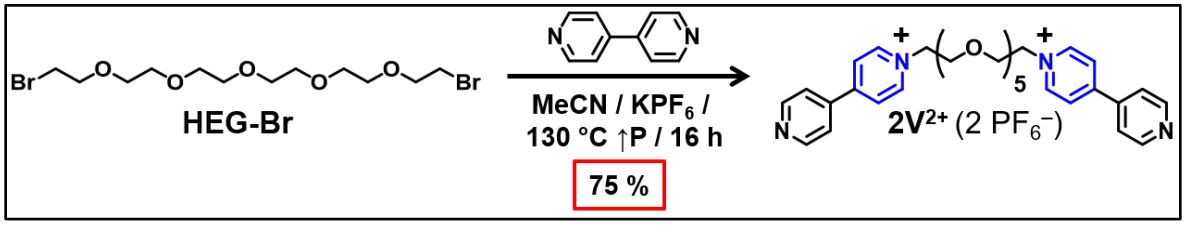
8) Zinc (4-(10,15,20-Triphenylporphyrin-5-yl)Phenoxy)Tetraethylene Glycol Acrylate (ZP-PC)



TPP-TEG-Acrylate (0.4 g, 0.46 mmol, 1 equiv), and $Zn(OAc)_2$ (0.85 g, 4.6 mmol, 10 equiv) were taken in a (7:3) $CHCl_3$: MeOH mixture (15 mL) and stirred overnight in darkness. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with H_2O (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation to yield the desired product, **ZP-PC**, as a purple solid (0.26 g, 95 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.94 (m, 8H); 8.22 (m, 6H); 8.11 (m, 2H); 7.76 (m, 9H); 7.27 (m, 2H); 6.37 (m, 1H); 6.11 (dd, J_1 = 10.4 Hz, J_2 = 17.3 Hz, 1H);); 5.80 (m, 1H); 4.41-4.25 (m, 4H); 3.99 (m, 4H); 3.86-3.63 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.22, 158.55, 150.68, 150.36, 143.05, 135.55, 134.58, 132.15, 132.07, 131.11, 128.33, 127.60, 126.67, 121.19, 121.11, 121.08, 112.84, 70.91, 70.74, 70.68, 69.95, 69.18, 67.75, 63.75. MALDI-TOF calculated for $C_{55}H_{49}N_4O_6Zn$ (*m/z*) 925.294, found: 925.883 $[M+H]^+$.

9) $2V^{4+}$-St and $6V^{12+}$-St Crosslinkers

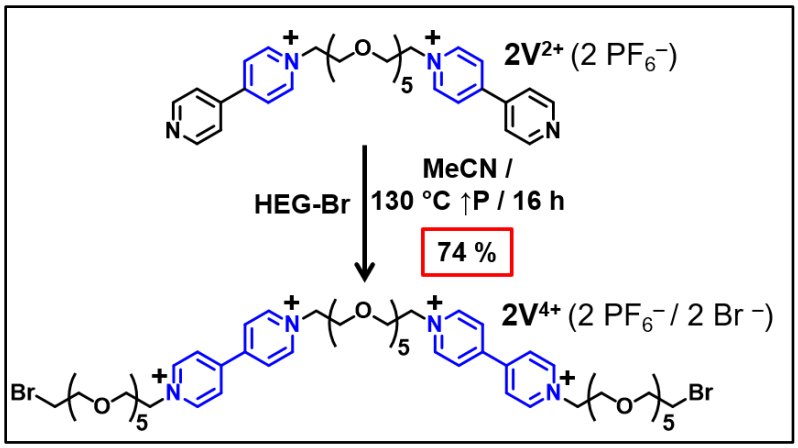
a) $2V^{2+}$



$2V^{2+}$ was synthesized according to the literature procedure reported by our group.[3] **HEG-Br** (3.7 g, 9.0 mmol, 1 equiv), potassium hexafluorophosphate (KPF_6) (5.0 g, 36.0 mmol, 3 equiv) and 4,4′-bipyridine (28.3 g, 181 mmol, 20 equiv) were dissolved in dry MeCN (50 mL) and the solution was added to a 100 mL thick-walled high-pressure flask with a Teflon screw cap and stir bar. The flask was capped tightly, and the mixture was heated to 130 °C and stirred for 16 h (high pressure). After 16 h, the solution was filtered using filter paper and transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL MeCN and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times to yield the desired product, **$2V^{2+}$** (as its $2PF_6^-$ salt), as a viscous, brown solid (5.8 g, 75 % yield). (Note: KPF_6 was added in this step as the PF_6^- counter anion increases the solubility of the resulting **$2V^{2+}$** product in MeCN, for efficient purification at this step and particularly in subsequent steps i.e. **$2V^{4+}$** and **$2V^{4+}$-St**). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.14 (d, J = 6.7 Hz, 4H); 8.87 (d, J = 5.9 Hz, 4H); 8.61 (d, J = 6.7 Hz, 4H); 8.02 (d, J = 6.0 Hz, 4H); 4.81 (m, 4H); 3.93 (m, 4H); 3.54 (m, 4H);); 3.55-3.38 (m, 12H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 152.54, 151.00, 145.77, 140.84, 125.02, 121.90, 69.69, 69.65, 69.51, 69.46, 68.57, 59.94. MALDI-TOF calculated for $C_{32}H_{40}F_{12}N_4O_5P_2$

[$2V^{2+}$•$2PF_6^-$] (*m/z*) 705.264, found 705.269 [*M*]; $C_{32}H_{40}N_4O_5^+$ [$2V^{2+}$+e^-] (*m/z*) 560.300, found 560.521 [$M+e^-$].

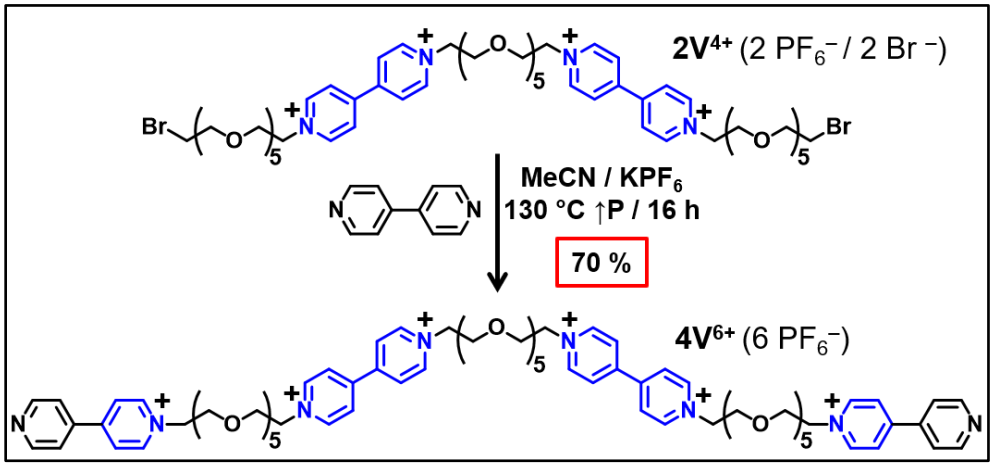
b) $2V^{4+}$



$2V^{2+}$ (as its 2 PF_6^- salt), (4.0 g, 4.7 mmol, 1 equiv) and **HEG-Br** (38.4 g, 94.0 mmol, 20 equiv), were dissolved in dry MeCN (400 mL, ≈ 10 mg/mL **$2V^{2+}$**) and the solution was added to six-100 mL (total volume must not exceed ≈ 65 mL in each flask) thick-walled high-pressure flasks with Teflon screw cap and stir bar. The flasks were capped tightly, and the mixture was heated to 130 °C and stirred for 16 h (high pressure). After 16 h, the reaction mixture was cooled to RT and the solution was filtered using filter paper. The filtrate was concentrated by rotary evaporation and transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL MeCN and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **$2V^{4+}$** (as its 2 PF_6^- / 2 Br^- salt), as a brown solid (6.25 g, 74 % yield). (Note: KPF_6 was not added in this step as the terminal hexaethylene glycol chains increase the solubility of the **$2V^{4+}$**

product in MeCN, for efficient purification). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.32 (m, 8H); 8.79 (m, 8H); 4.89 (m, 8H); 3.98 (m, 8H); 3.70 (m, 4H); 3.63-3.41 (m, 48H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 148.94, 148.87, 146.22, 146.18, 126.33, 126.30, 72.29, 70.33, 69.77, 69.69, 69.55, 68.61, 60.52. MALDI-TOF calculated for $C_{56}H_{88}Br_3Cl_2N_4O_{15}$ [$2V^{4+}$•Br^-•$2Cl^-$+e^-] (m/z) 1363.327, found 1362.507[M^+•Br^-•$2Cl^-$+e^-].

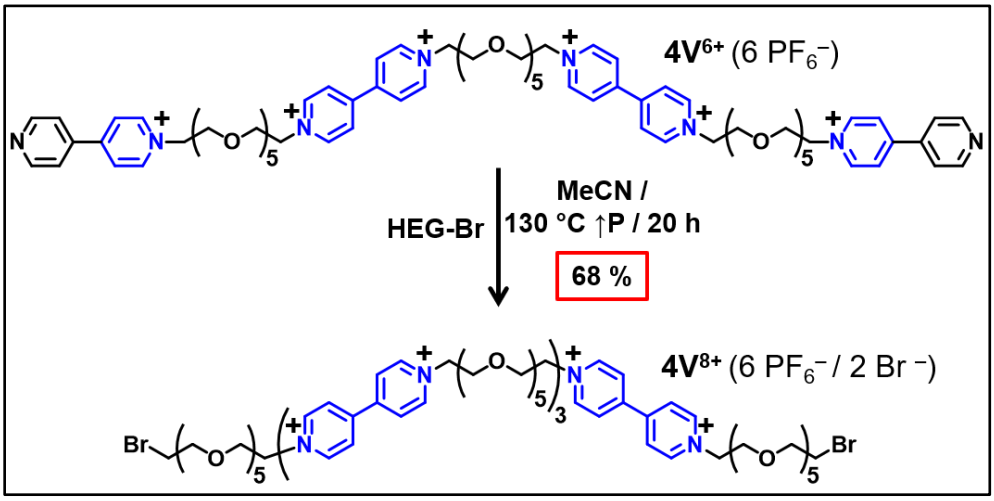
c) $4V^{6+}$



$2V^{4+}$ (as its 2 PF_6^- / 2 Br^- salt) (6.1 g, 3.3 mmol, 1 equiv) was dissolved in dry MeCN (600 mL, ≈ 10 mg/mL **$2V^{4+}$**) and the solution was added (equally) to nine-100 mL (total volume must not exceed ≈ 65 mL in each flask) thick-walled high-pressure flasks with Teflon screw cap and stir bar. KPF_6 (2.43 g, 13.2 mmol, 4 equiv) and 4,4′-bipyridine (10.6 g, 67.8 mmol, 20 equiv), were evenly added to the flasks. The flasks were capped tightly, and the mixture was heated to 130 °C and stirred for 16 h (high pressure). After 16 h, the reaction mixture was cooled to RT and the solution was filtered using filter paper. The filtrate was concentrated by rotary evaporation and transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min.

The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL MeCN and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **4V^{6+}** (as its 6 PF_6^- salt), as a brown solid (5.3 g, 70 % yield). (Note: KPF_6 was added in this step as the PF_6^- counter anion increases the solubility of the resulting **4V^{6+}** product in MeCN, for efficient purification). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.32 (m, 8H); 9.17 (m, 4H); 8.87 (m, 4H); 8.79 (m, 8H); 8.64 (m, 4H); 8.04 (m, 4H); 4.87 (m, 12H); 3.96 (m, 12H); 3.69-3.40 (m, 48H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 152.54, 151.00, 145.77, 140.84, 125.02, 121.90, 69.69, 69.65, 69.51, 69.46, 68.61, 59.94.

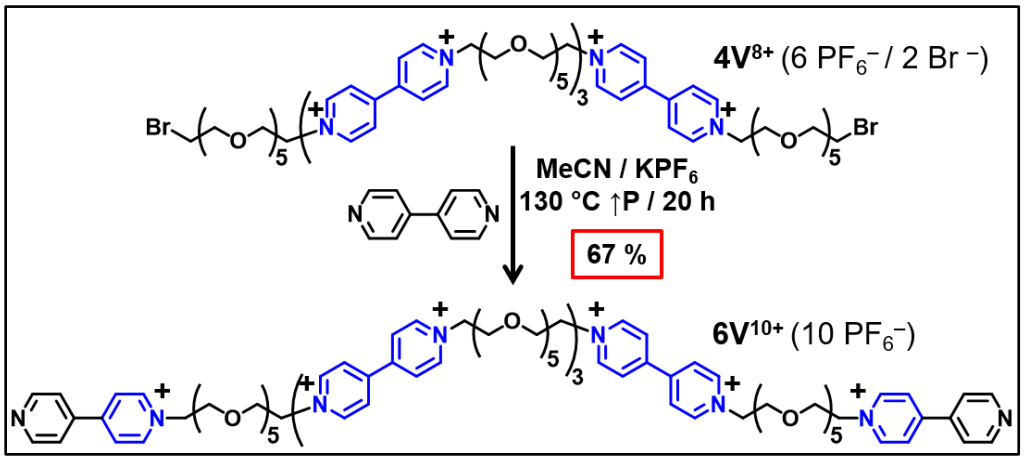
d) 4V^{8+}



4V^{6+} (as its 6 PF_6^- salt) (5.2 g, 2.3 mmol, 1 equiv) and **HEG-Br** (18.9 g, 46.4 mmol, 20 equiv), were dissolved in dry MeCN (520 mL, ≈ 10 mg/mL **4V^{8+}**) and the solution was added to eight-100 mL (total volume must not exceed ≈ 65 mL in each flask) thick-walled high-pressure flasks with Teflon screw cap and stir bar. The flasks were capped tightly, and the mixture was heated to 130 °C and stirred for 20 h (high pressure). After 20 h, the reaction mixture was cooled to RT and the

solution was filtered using filter paper. The filtrate was concentrated by rotary evaporation and transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL MeCN and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **4V**$^{8+}$ (as its 6 PF_6^- / 2 Br^- salt) as a brown solid (5.0 g, 68 % yield). (Note: KPF_6 was not added in this step as the terminal hexaethylene glycol chains increase the solubility of the resulting **4V**$^{8+}$ product in MeCN, for efficient purification). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.32 (m, 16H); 8.80 (m, 16H); 4.89 (m, 16H); 3.98 (m, 16H); 3.70 (m, 4H); 3.62-3.40 (m, 80H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 150.84, 148.88, 146.45, 146.18, 126.33, 126.31, 72.29, 70.31, 69.76, 69.67, 69.49, 68.61, 60.41.

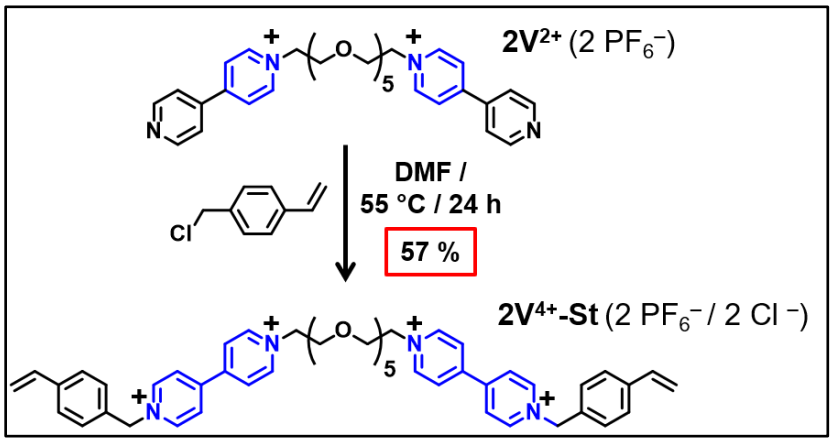
e) 6V^{10+}



4V^{8+} (as its 6 PF_6^- / 2 Br^- salt) (4.9 g, 1.5 mmol, 1 equiv) was dissolved in dry MeCN (490 mL, ≈ 10 mg/mL **2V**$^{4+}$) and the solution was added (equally) to eight-100 mL (total volume must not exceed ≈ 65 mL in each flask) thick-walled high-pressure flasks with Teflon screw cap and stir bar. KPF_6 (1.1 g, 6.0 mmol, 4 equiv) and 4,4′-bipyridine (4.8 g, 30.7 mmol, 20 equiv), were evenly

added to the flasks. The flasks were capped tightly, and the mixture was heated to 130 °C and stirred for 20 h (high pressure). After 20 h, the reaction mixture was cooled to RT and the solution was filtered using filter paper. The filtrate was concentrated by rotary evaporation and transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL MeCN and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **6V^{10+}** (as its 10 PF_6^- salt) as a brown solid (3.7 g, 67 % yield). (Note: KPF_6 was added in this step as the PF_6^- counter anion increases the solubility of the resulting **6V^{10+}** product in MeCN, for efficient purification). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.35 (m, 16H); 9.18 (m, 4H); 8.85 (m, 20H); 8.65 (m, 4H); 8.04 (m, 4H); 4.87 (m, 20H); 3.97 (m, 20H); 3.65-3.40 (m, 80H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 152.50, 150.98, 145.78, 140.86, 125.03, 121.93, 69.70, 69.65, 69.52, 69.48, 68.64, 59.92.

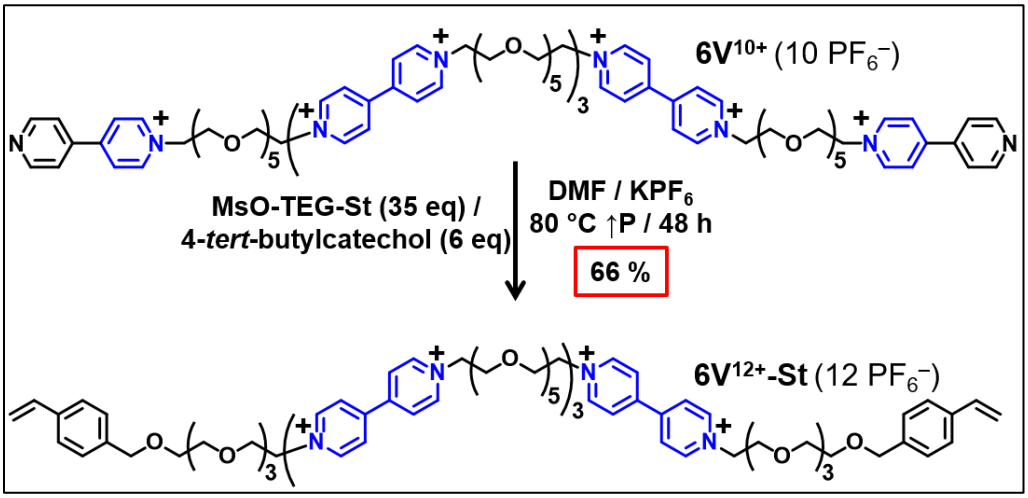
f) 2V^{4+}-St



2V^{4+}-St was synthesized according to the literature procedure reported by our group[2]. **2V^{2+}** (as its 2 PF_6^- salt) (2.0 g, 2.3 mmol, 1 equiv) and 4-vinylbenzyl chloride (17.9 g, 117 mmol, 50 equiv)

were dissolved in dry DMF (26.6 mL, 75 mg/mL **2V^{2+}**) and heated to 55 °C for 24 h. After 24 h, MeOH (10 mL) was added to the solution to dissolve the precipitate and the solution was transferred to four 50 mL centrifuge tubes and diluted with 40 mL PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was redissolved in 5 mL DMF and 45 mL PhMe: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **2V^{4+}-St** (as its 2 PF_6^- / 2 Cl^- salt) as a brown solid (1.5 g, 57 % yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.48 (d, 4H), 9.28 (d, 4H), 8.73 (dd, J_1 = 6.9 Hz, J_2 = 11.6 Hz, 8H), 7.58 (m, 8H), 6.76 (dd, J_1 = 10.9 Hz, J_2 = 17.7 Hz, 2H), 5.93 (s, 4H), 5.90 (d, J = 17.7 Hz, 2H), 5.33 (d, J = 11.0 Hz, 2H), 4.87 (m, 4H), 3.97 (m, 4H), 3.56 (m, 4H), 3.40-3.50 (m, 12H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 149.16, 148.97, 145.09, 145.64, 138.31, 135.72, 133.40, 129.27, 127.11, 126.86, 126.33, 115.82, 69.63, 69.44, 68.55, 64.86, 63.26, 60.45. MALDI-TOF calculated for $C_{50}H_{58}Cl_2N_4O_5$ (2V^{4+}-St•2Cl$^-$•e$^-$) (*m/z*) 867.379, found 867.579 [*M*+*e*$^-$]; calculated for $C_{57}H_{65}N_4O_8S$ (2V^{4+}-St•TsO+2e$^-$) (*m/z*) 965.452, found 965.5 [*M*+2*e*$^-$].

g) 6V^{12+}-St



6V^{10+} (as its 10 PF_6^- salt) (3.65 g, 1.0 mmol, 1 equiv), 4-*tert*-butylcathecol (1.0 g, 6.0 mmol, 6 equiv), **MsO-TEG-St** (13.6 g, 35.2 mmol, 35 equiv) and KPF_6 (0.55 g, 3.0 mmol, 3 equiv) were dissolved in dry DMF (48 mL, 75 mg/mL **6V^{10+}**) and heated to 80 °C for 48 h in a 100 mL thick-walled high-pressure flask. After 48 h, the reaction mixture was cooled to RT and diluted with MeOH (30 mL) and filtered and concentrated by rotary evaporation. The product transferred to eight-50 mL centrifuge tubes (5 mL in each tube) and diluted to 50 mL with PhMe: Et_2O (1:2) to precipitate the product. The tubes were centrifuged at 4500 rpm at –10 °C for 30 min. The resulting supernatant was decanted, the dark brown oil was re-dissolved in 5 mL DMF, and 45 mL THF: Et_2O (1:2) was added, followed by centrifugation. This process was repeated four times and the resulting viscous, brown solid, was dried *in vacuo* overnight to yield the desired product **6V^{12+}-St** (as its 12 PF_6^- salt) as a brown solid (2.9 g, 66 % yield). (Note: KPF_6 was added in this step as the PF_6^- counter anion increases the solubility of the resulting **6V^{12+}-St** product in MeCN, for efficient purification). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 9.31 (m, 24H), 8.79 (m, *2*4H), 7.40 (d, *J* = 7.9 Hz, 4H), 7.24 (d, *J* = 7.8 Hz, 4H), 6.70 (dd, *J* = 10.9, 17.6 Hz, 2H), 5.79 (d, *J* = 17.7 Hz, 2H), 5.24 (d, *J* = 10.9 Hz, 2H), 4.89 (m, 24H), 4.43 (m, 4H), 3.98 (m, 24H), 3.65-3.4 (m, 104H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 148.86, 148.81, 146.22, 138.05, 136.29, 136.23, 127.73, 126.34, 126.28, 126.25, 125.97, 114.16, 71.68, 69.77, 69.59, 69.10, 68.66, 64.88, 60.38. MALDI-TOF calculated as $C_{156}H_{224}F_{60}N_{12}O_{39}P_{10}S_2$ ($6V^{12+}$-St•$10PF_6^-$•$2MsO^-$) (*m/z*) 4410.19, found 4410.2 [*M*].

Section C. Spectroscopic Characterization

1) Nuclear Magnetic Resonance (^{1}H and ^{13}C)

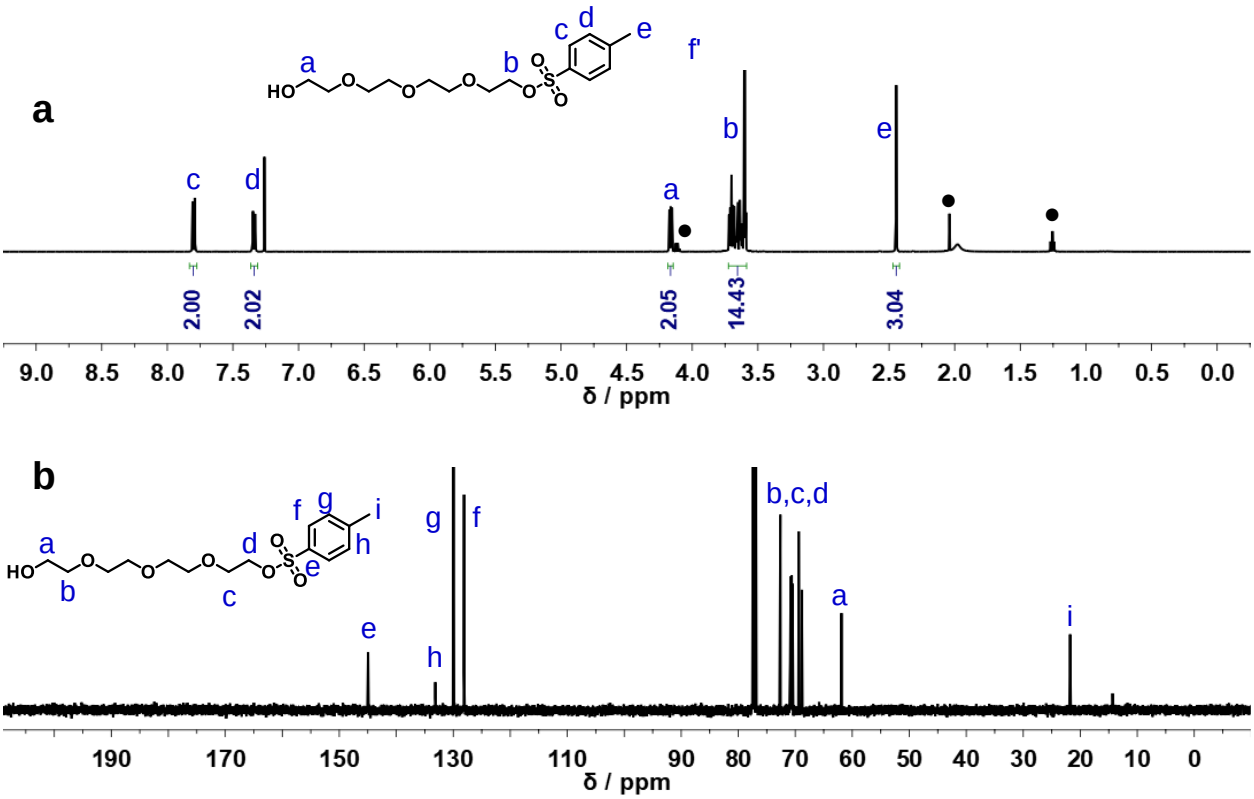


Figure S1: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **HO-TEG-OTs** recorded in $CDCl_3$ at 298K. ● EtOAc

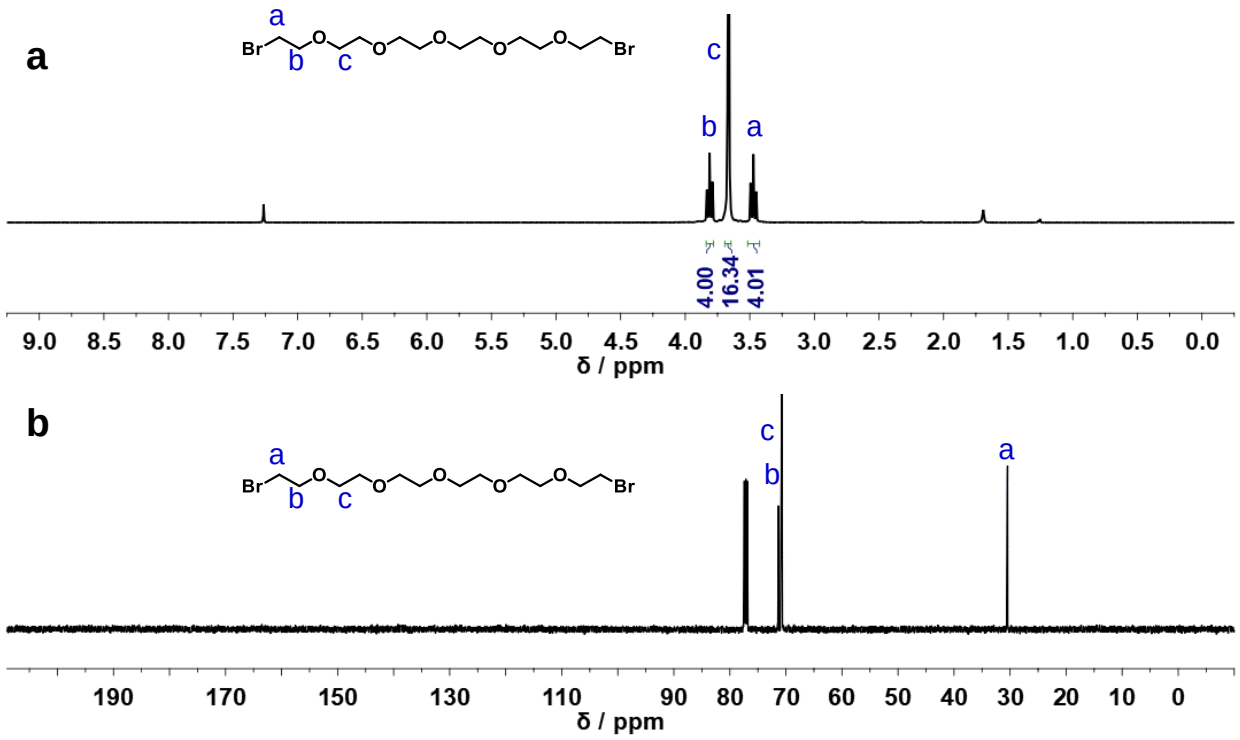


Figure S2: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **HEG-Br** recorded in $CDCl_3$ at 298K.

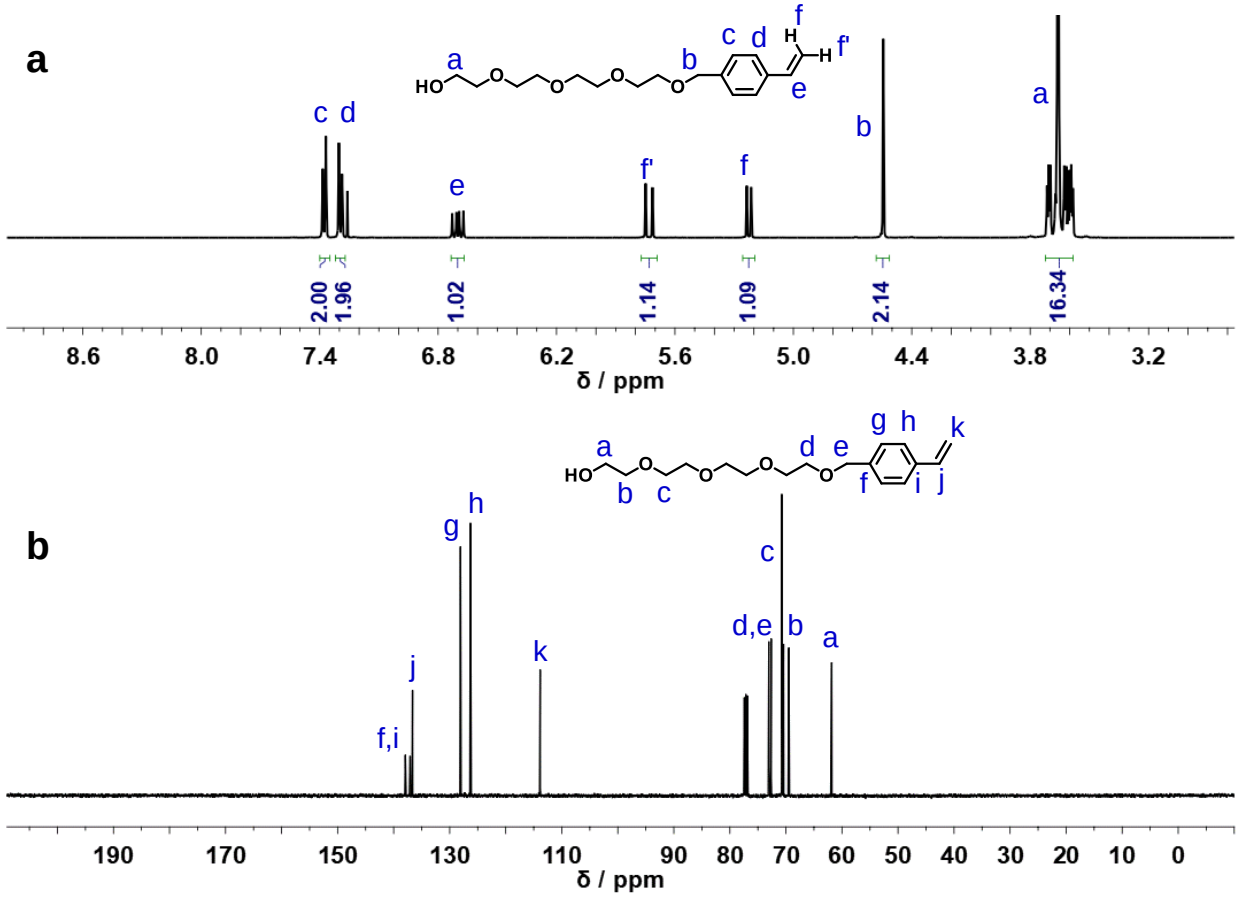


Figure S3: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **HO-TEG-St** recorded in $CDCl_3$ at 298K.

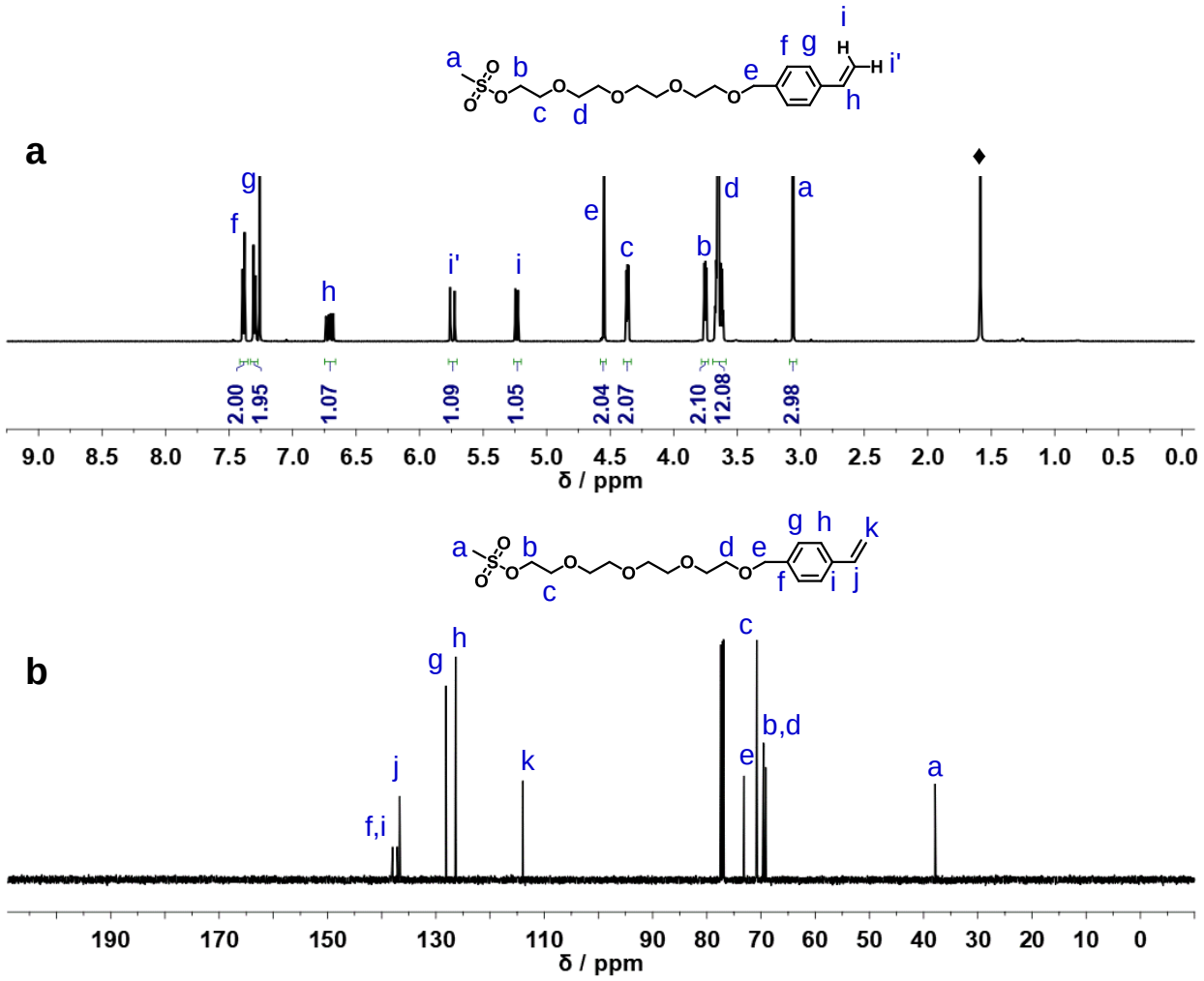


Figure S4: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **MsO-TEG-St** recorded in $CDCl_3$ at 298K. ♦H_2O

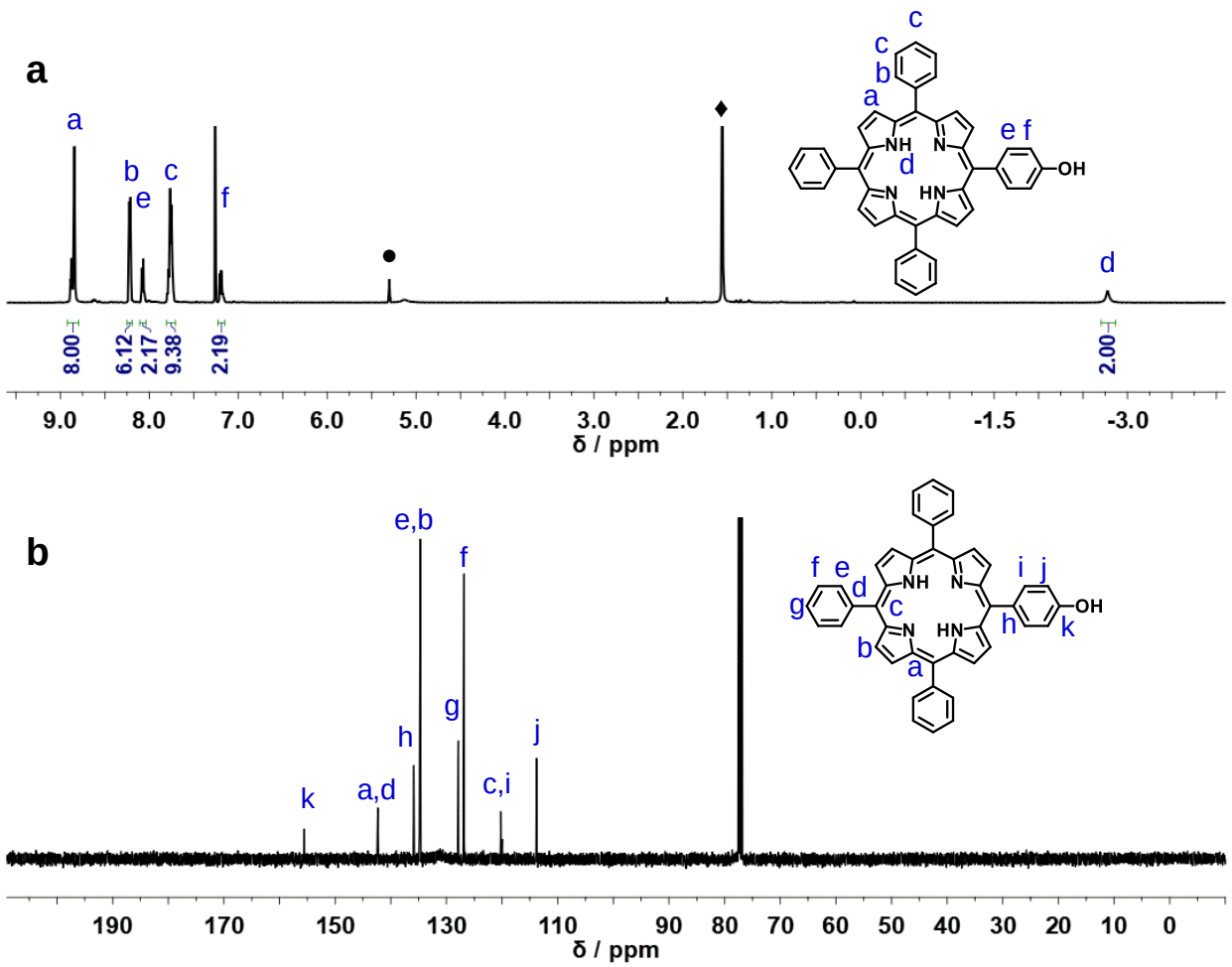


Figure S5: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **TPP−OH** recorded in $CDCl_3$ at 298K. ●CH_2Cl_2 ♦H_2O.

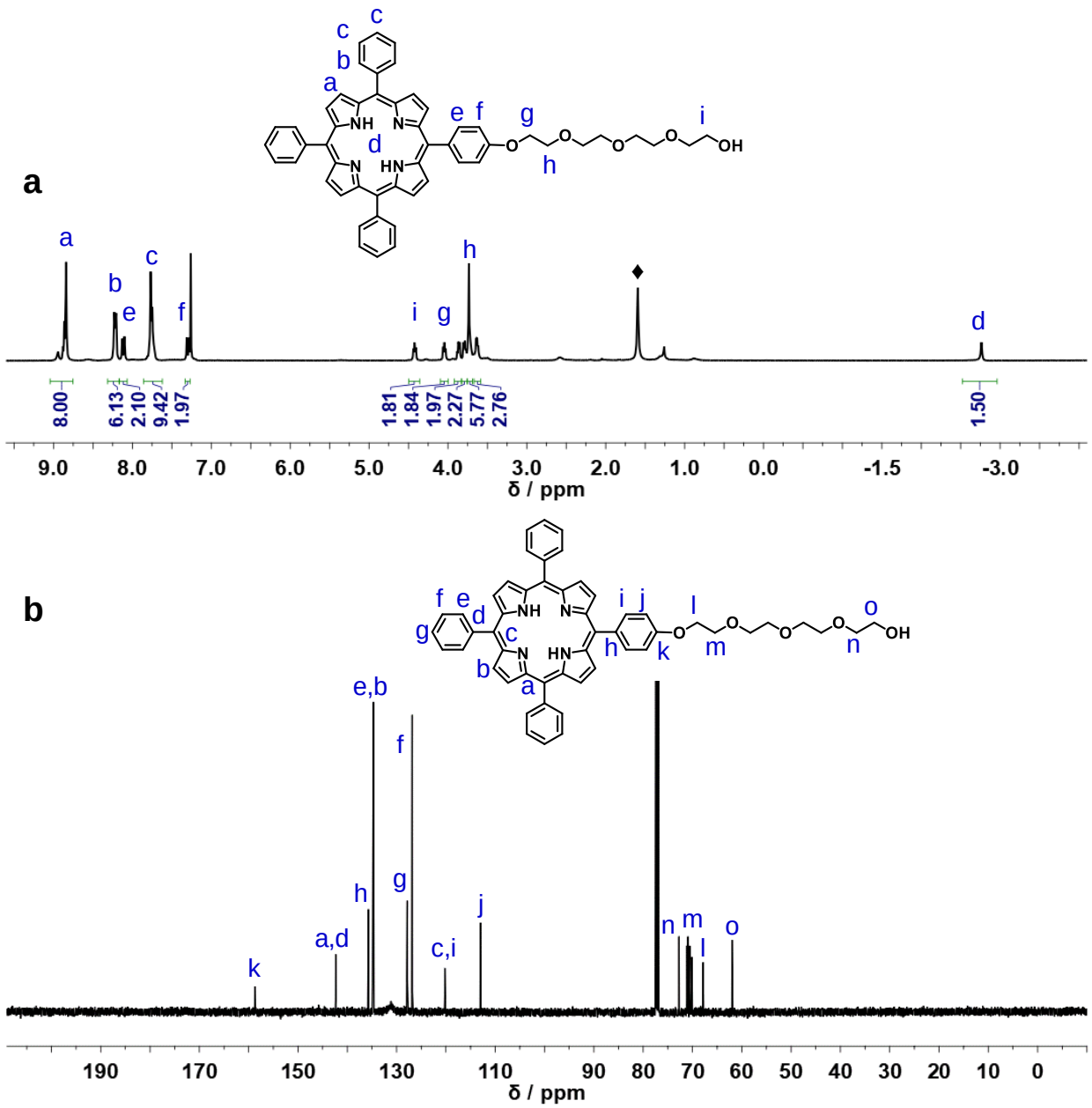


Figure S6: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **TPP-TEG-OH** recorded in $CDCl_3$ at 298K. ♦H_2O.

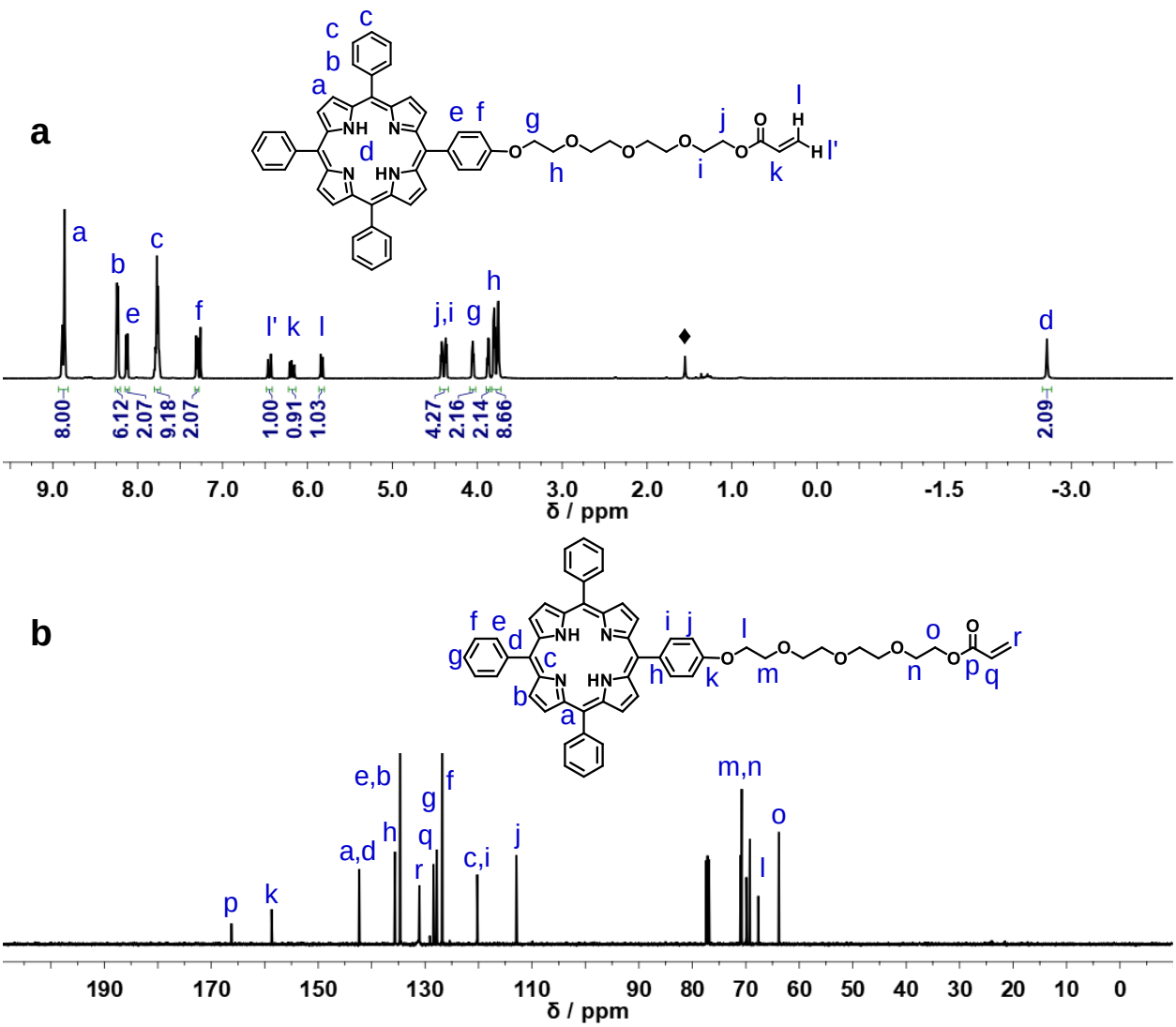


Figure S7: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **TPP-TEG-Acrylate** recorded in $CDCl_3$ at 298K. ♦H_2O.

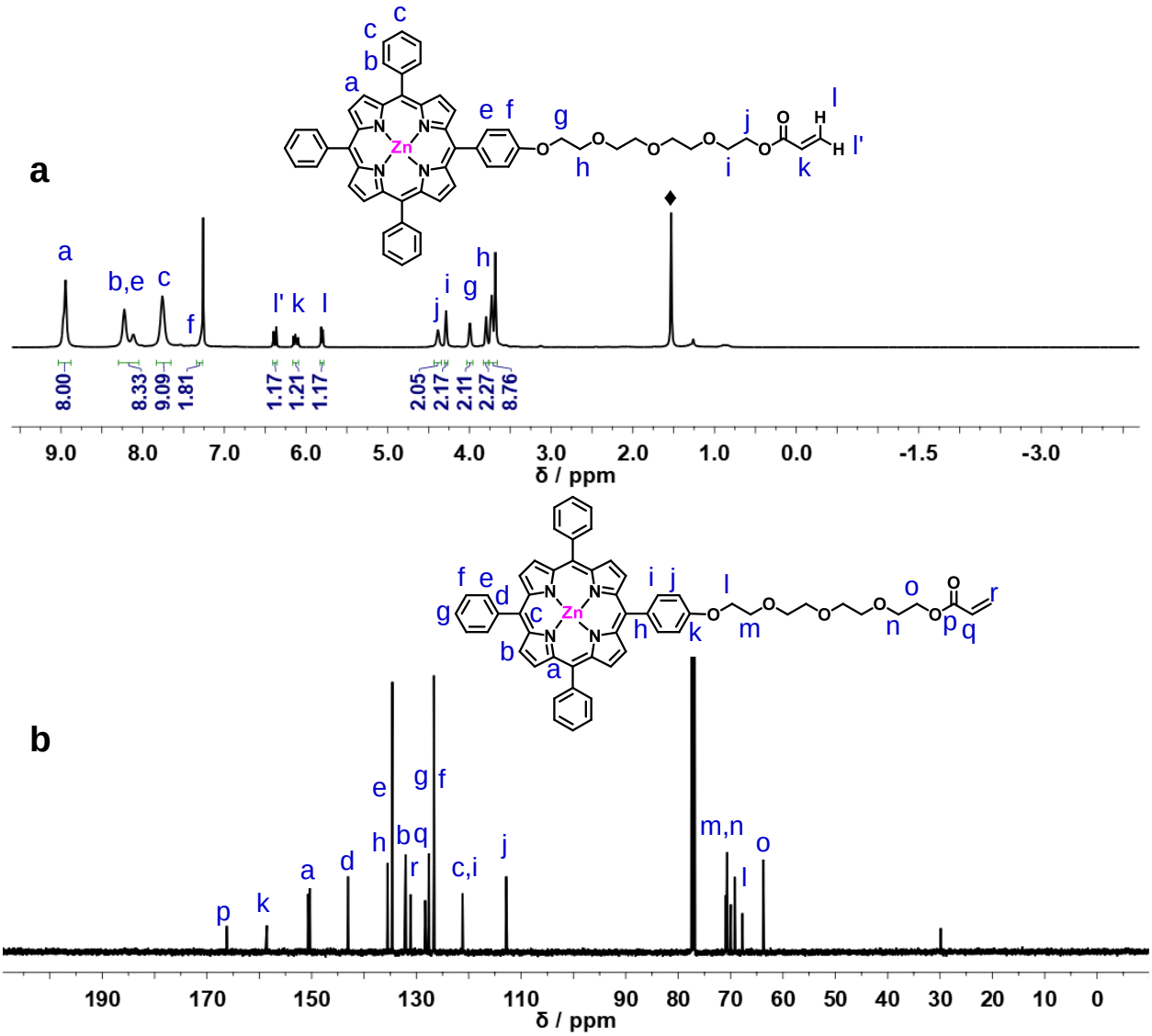


Figure S8: a) ^{1}H NMR (500 MHz) and **b**) ^{13}C NMR (125 MHz) of **ZP-PC** recorded in $CDCl_3$ at 298K. ♦H_2O

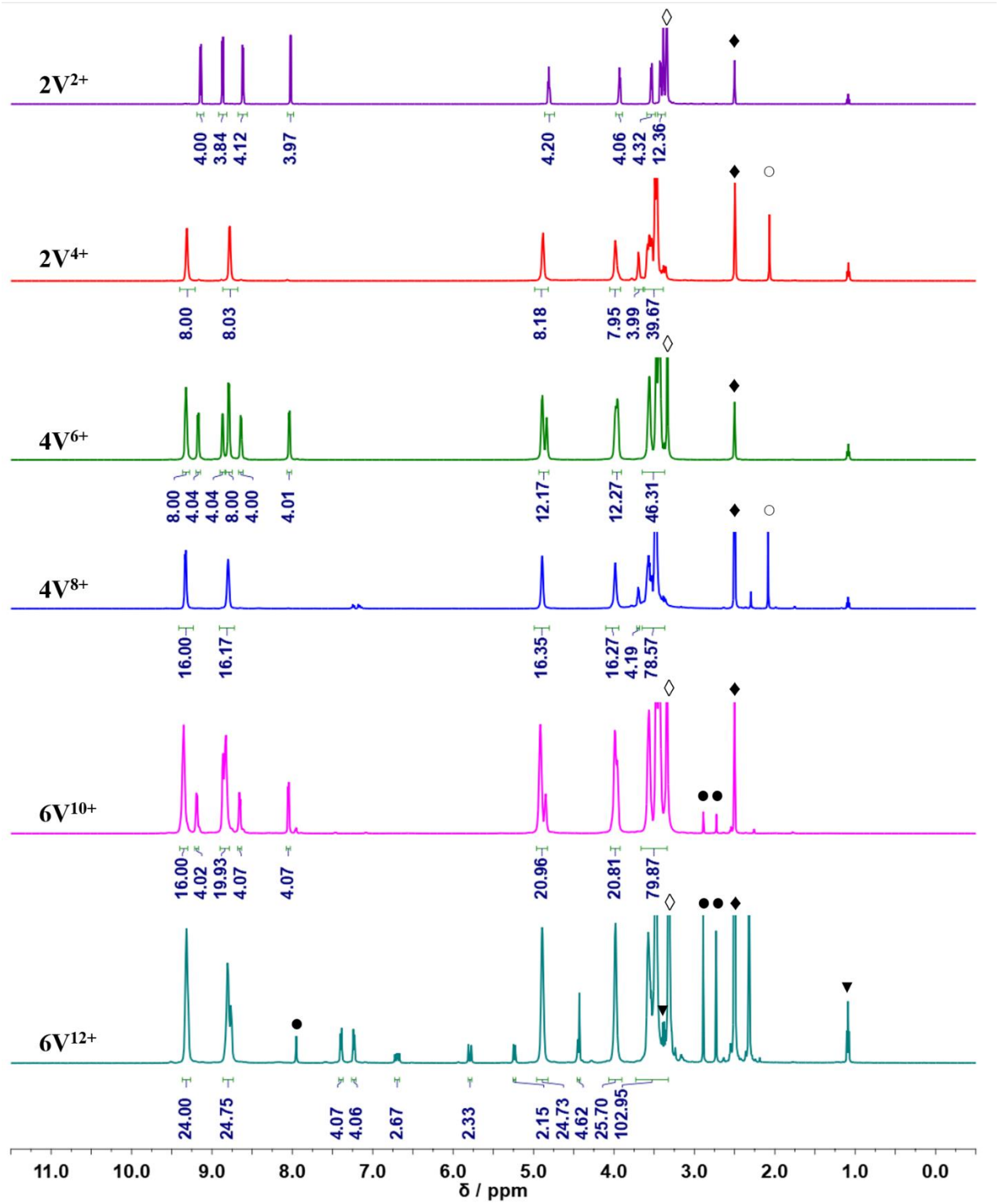


Figure S9: ^{1}H NMR (500 MHz, $(CD_3)_2SO$) spectra for each iterative product in the synthesis of the crosslinker (**6V^{12+}-St**•12PF_6^-) used to fabricate the hydrogels. ●DMF ♦DMSO ◊H_2O ▼Et_2O ○MeCN.

2) UV-Vis-NIR Absorption

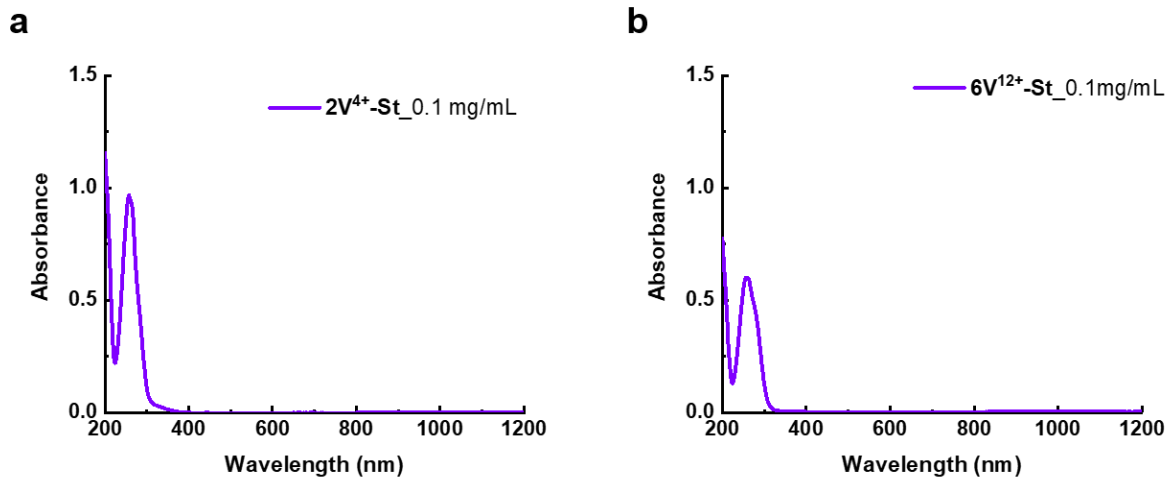


Figure S10: UV-Vis characterization of **a**) **$2V^{4+}$-St** and **b**) **$6V^{12+}$-St** in MeCN.

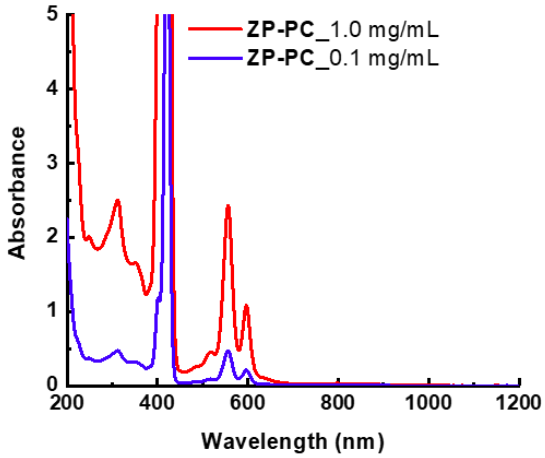


Figure S11: UV-Vis characterization of **ZP-PC** in MeCN at different concentrations.

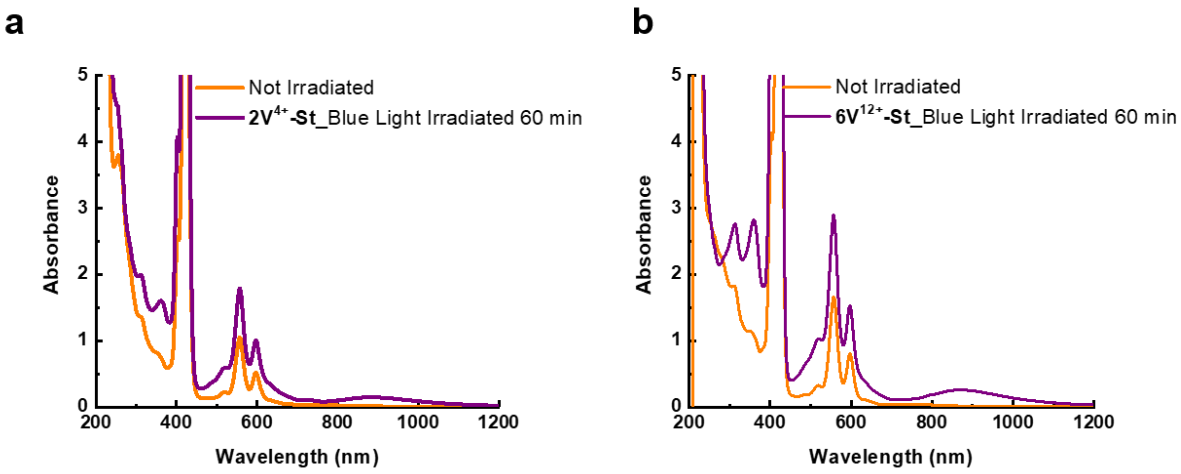


Figure S12: UV-Vis-NIR absorption spectroscopic characterization of a solution containing **a**) 0.25 mM **$2V^{4+}$-St**, 0.3 mM **ZP-PC**, and 3.0 mM TEOA and **b**) 0.25 mM **$6V^{12+}$-St**, 0.3 mM **ZP-PC**, and 3.0 mM TEOA before and after irradiation with Blue Light.

3) Size Exclusion Chromatography

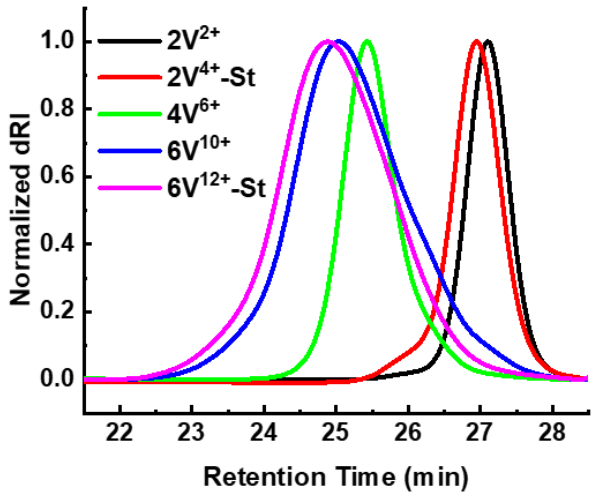


Figure S13: Size exclusion chromatography (SEC) differential refractive index (dRI) traces of pyridyl-terminated intermediates and final styrene-capped oligoviologen product. Each sample was prepared as its bisulfate salt (HSO_4^-) from PF_6^- by addition of a drop of concentrated H_2SO_4 into a viologen sample dissolved in 0.025 M solution of Na_2SO_4 in H_2O, followed by running each in an aqueous mobile phase with 0.025 M Na_2SO_4 at 23 °C with 1.0 mL/min flow ratio.

Section D. Gel Preparation, Photochemical Reduction, Actuation, and Evaluation of Mechanical Properties

1) General Procedure for the Preparation of Hydrogels

Hydrogels were synthesized according to the literature procedure reported by our group.[6, 7] For each gel, the reagents for polymerization (**Table S1**) were dissolved in 1.107 mL of DMSO and the solution was vortexed and sonicated to ensure complete dissolution and even mixing. The solution was then plated into a 2.0 cm diameter, disc shaped rubber septum (1.5 mL/mold) and heated in an oven at 80 °C for 1 h. The cured gels were carefully removed from the gel mold using a spatula and placed in a solvent-resistant plastic box. The gels were then soaked in H_2O for 48 h to allow for full swelling. FTIR was performed on a separate, as-synthesized gel to confirm complete conversion of the crosslinker (**Figure S14**). **Figure S15** shows the gels synthesized and swollen in H_2O for 48 h. A 20 mm disc was punched out of the swollen gels and the rheological data (**Figure S19** and **S20**) was acquired.

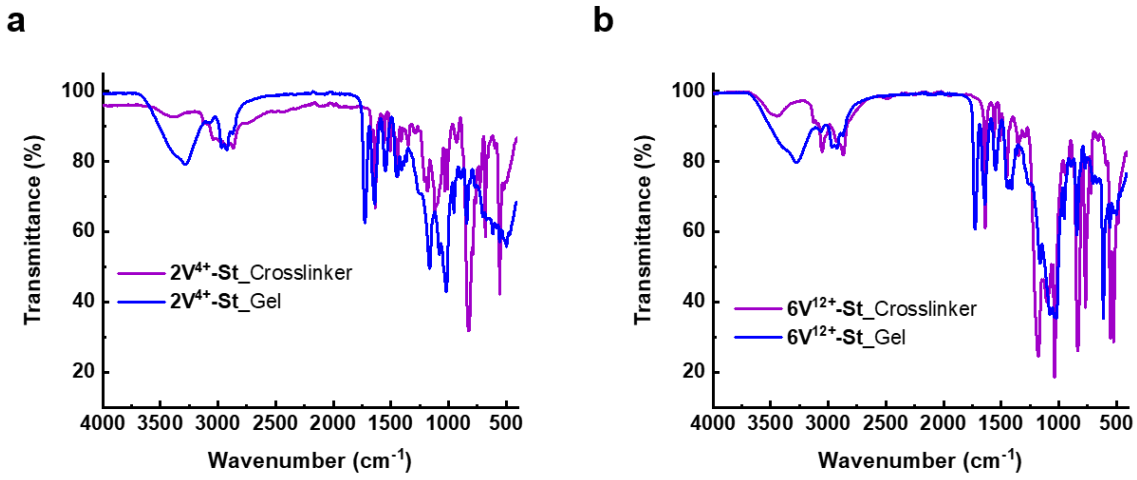


Figure S14: FTIR of **a**) **$2V^{4+}$-St** crosslinker and **$2V^{4+}$-St** crosslinked **(**as-synthesized) gel and **b**) **$6V^{12+}$-St** crosslinker and **$6V^{12+}$-St** crosslinked **(**as-synthesized) gel. The disappearance of the sp^2 CH stretch between 3000 and 3150 cm^{-1} and the C=C stretch at 1640 cm^{-1} indicates complete conversion of the crosslinker.

Table S1: Reagents used for the synthesis of four gels containing 0.37 mol % **6V^{12+}-St** and **2V^{4+}-St** crosslinkers. 2-hydroxyethyl acrylate (HEA), ammonium persulfate (APS), *N*-isopropylacrylamide (NiPAM).

Crosslinker mol %	(**6V^{12+}-St) 0.37 mol %**	(**2V^{4+}-St) 0.37 mol %**
HEA (mg)	227.4	251.1
NiPAM (mg)	151.6	167.4
Crosslinker (mg)	55.0	15.5
ZnTPP-TEG-Acrylate (mg)	4.4	4.4
Ammonium Persulfate (mg)	5.0	5.0
HEA (mol %)	59	59
NiPAM (mol %)	40	40
Total mass (mg)	443.4	443.4
DMSO (mL)	1.107	1.107

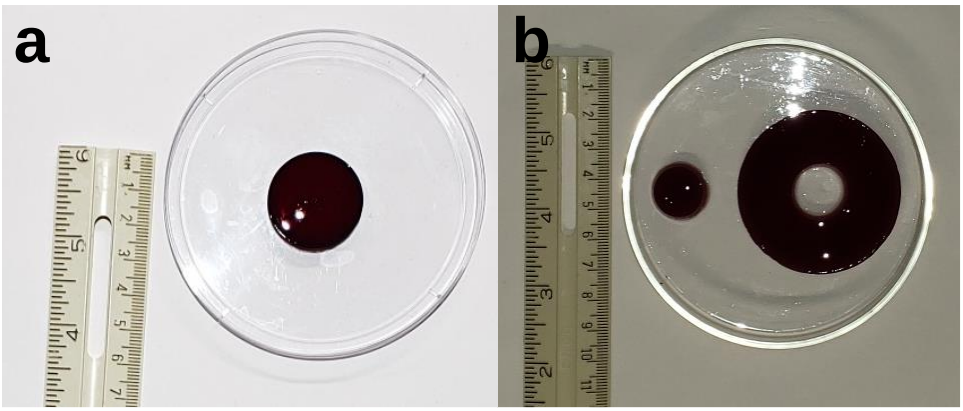


Figure S15: a) **6V^{12+}-St** crosslinked as-synthesized gel and **b**) **6V^{12+}-St** crosslinked swollen as-synthesized gel.

2) Photochemical Reduction of Gels: Procedure, Kinetics, and Rheology

All kinetics experiments were performed in triplicate inside of an N_2-filled glovebox, even though photoreduction does work on the bench under ambient conditions. The gels were prepared as described above and were swollen for an additional 24 h in a degassed solution of 3.00 mM TEOA in H_2O inside the glovebox. The average (n = 3) gel volume at t = 0 was 6.28 cm^3 for the **$2V^{4+}$-St** crosslinked gels and 7.26 cm^3 for the **$6V^{12+}$-St** crosslinked gels, respectively. The gels were then removed from solution and placed in a 14 cm diameter glass petri dish. A water-soaked Kimwipe was also placed inside the petri dish, which was covered by a lid to ensure proper hydration during photoirradiation. The gels were irradiated with ~450 nm (blue light) or ~620 nm (red light) from the top and bottom for 5 h, maintaining a 5.5 cm distance between the gel and the light source (**Figure S16**) with volume measurements taken at regular intervals (**Figure S18**). After irradiation, the gels were removed from the light source and punched to yield a 20 mm diameter disc-like gel. The resulting gel discs were placed into an airtight container and transported for rheological experiments, which were performed to obtain rheological data on the reduced/contracted gels (Figure **S19 a** and **c**, **S20 a** and c). The resulting discs were oxidized and swollen in H_2O. A new 20 mm diameter disc was punched out from the resulting reswollen gels and the oxidized rheological data were recorded (**Figure S19 b** and **d**, **S20 b** and **d**). For the control, **$2V^{4+}$-St** and **$6V^{12+}$-St** crosslinked gels were synthesized in triplicates with no photocatalyst **(ZP-PC)** and the same protocol was repeated on the swollen triplicate set of hydrogels.

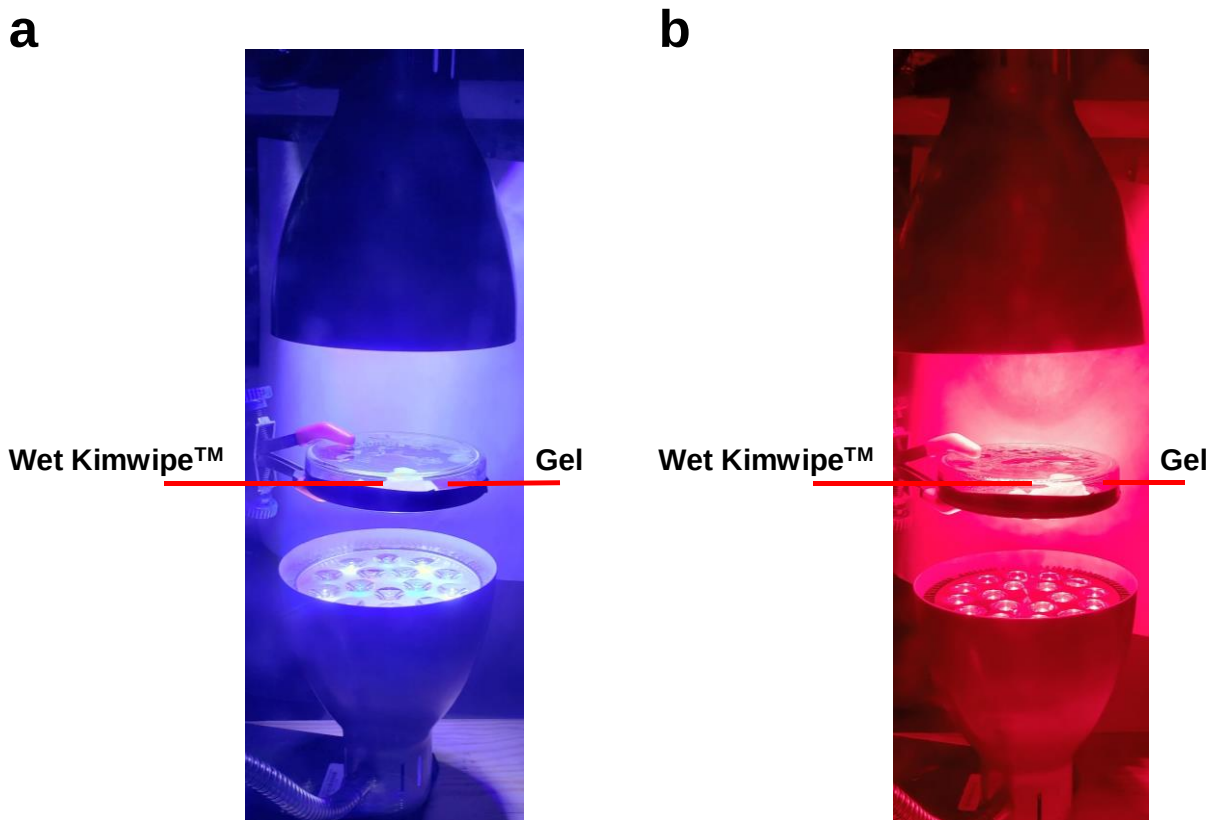


Figure S16: Experimental setup for photoirradiation experiments. Gels in a taped petri dish being irradiated from top and bottom approximately 5.5 cm away from: **a**) ~450 nm blue light source and **b**) ~660 nm blue light source.

3) Thermal Contraction of Gels: Procedure, Kinetics, and Rheology

The gels were prepared as described above, and all kinetics experiments were performed in triplicate. The average (n = 3) gel volume at t = 0 was 9.97 cm^3 for the **$2V^{4+}$-St** crosslinked gels and 11.31 cm^3 for the **$6V^{12+}$-St** crosslinked gels. The experimental setup for thermal contraction of hydrogels included three 250 mL beakers each containing 125 mL H_2O were placed in a large H_2O bath at 50°C. A small rubber septum was placed under each beaker to ensure uniform heating (**Figure S17**). The gels were placed in each of the beakers and volume measurements taken at regular intervals (**Figure S18**). After thermal contraction, the gels were removed from the heat source and a 20 mm diameter disc gel was punched out of the material. The gel discs were placed

into an airtight container and transported for rheological experiments, which were performed to obtain the reduced/contracted rheological data on the gels (**Figure S19** and **S20**).

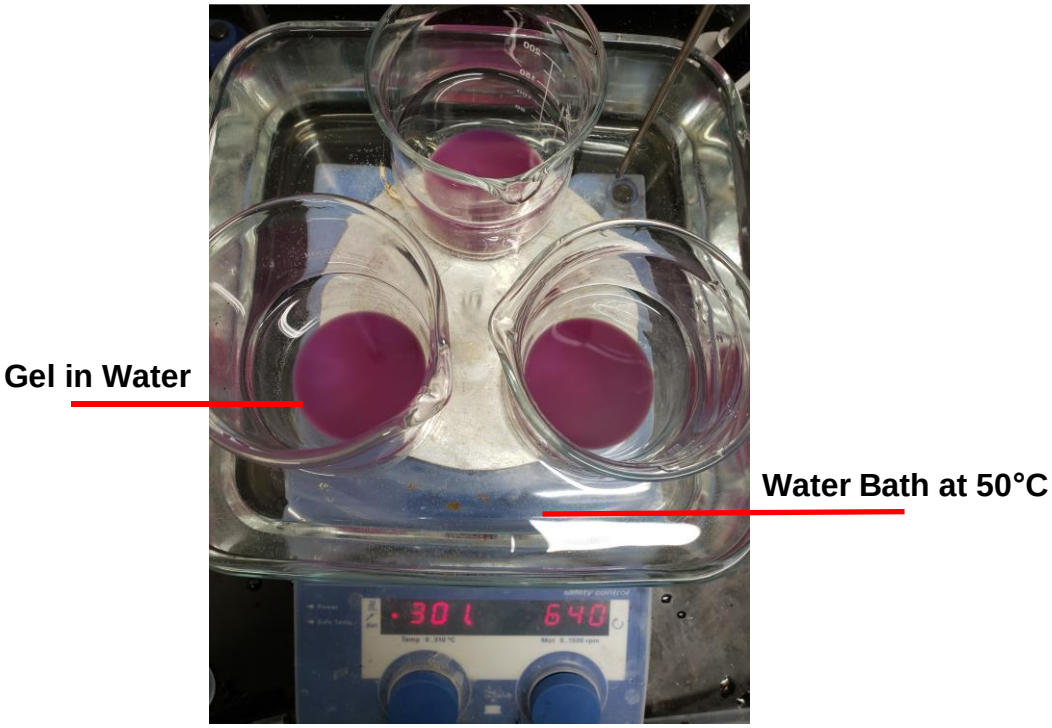


Figure S17: Experimental setup for Thermal contraction experiments. Gels in H_2O in 250 mL beaker heated at 50 °C.

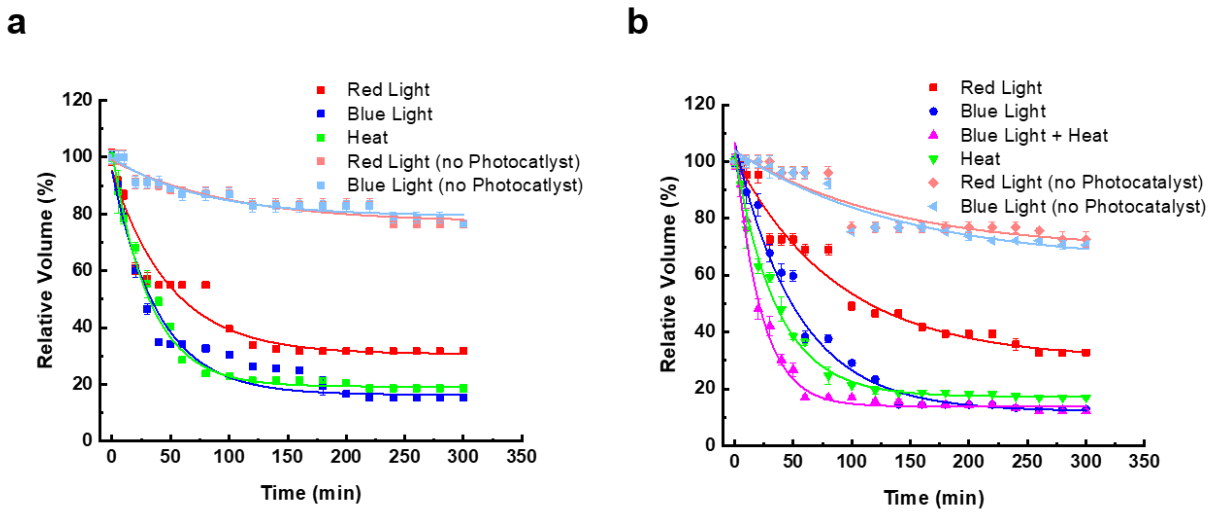


Figure S18: Kinetic plots of relative volume change of hydrogels composed of **a**) **$2V^{4+}$-St** and **b**) **$6V^{12+}$-St** crosslinked hydrogels activated by visible light (blue, 450 nm and red, 660 nm), heat (50 °C), and bimodal (blue light + heat).

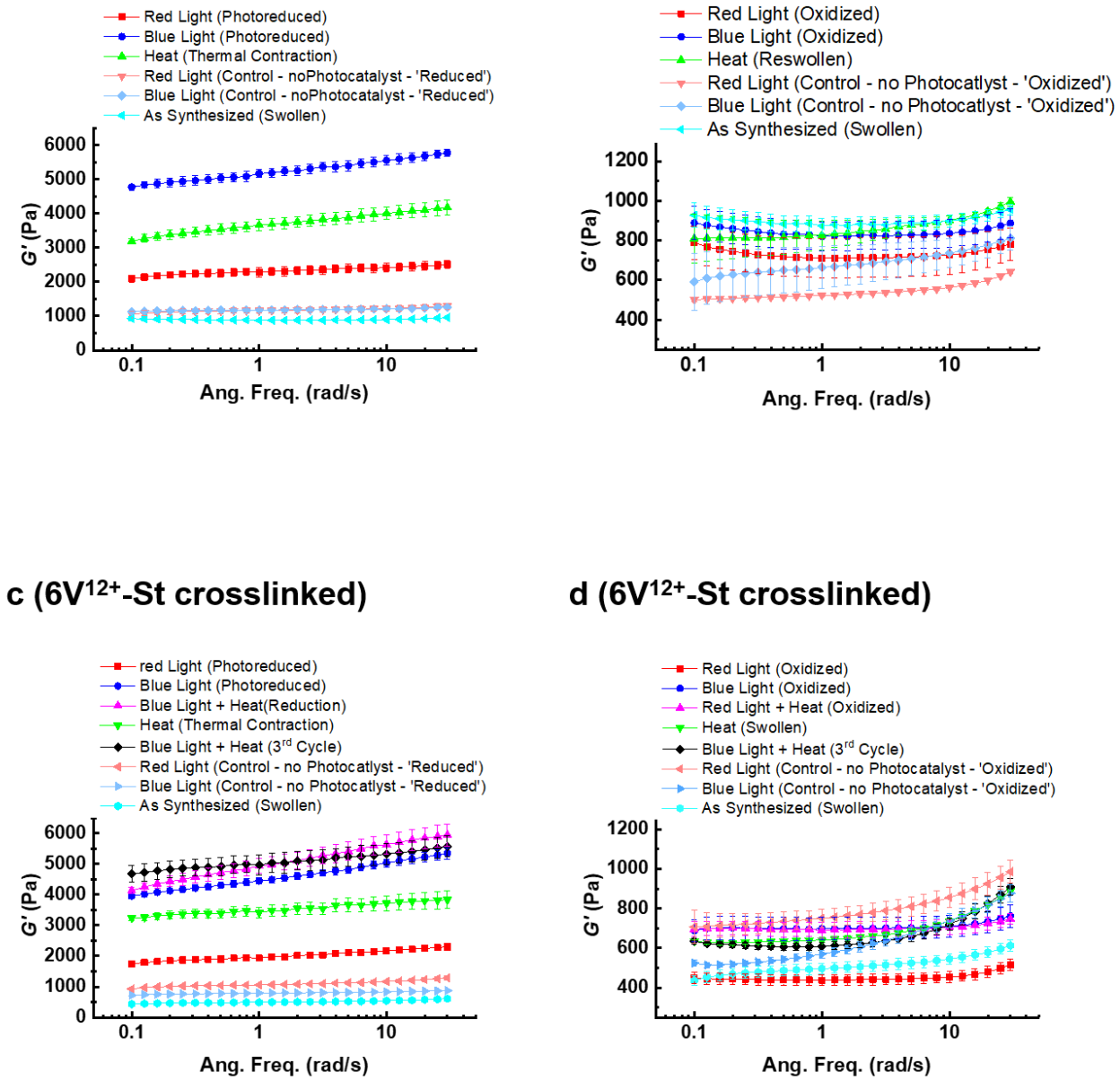


Figure S19: Oscillatory shear rheology data. **a**) Storage modulus (G') of the photoreduced and thermally-contracted **2V^{4+}-St** crosslinked hydrogels, **b**) Storage modulus (G') of the oxidized, re-swollen, and as-synthesized (swollen) **2V^{4+}-St** crosslinked hydrogels, **c**) Storage modulus (G') of the photoreduced and thermally-contracted **6V^{12+}-St** crosslinked hydrogels, **d**) Storage modulus (G') of the oxidized, re-swollen, and as-synthesized (swollen) **6V^{12+}-St** crosslinked hydrogels.

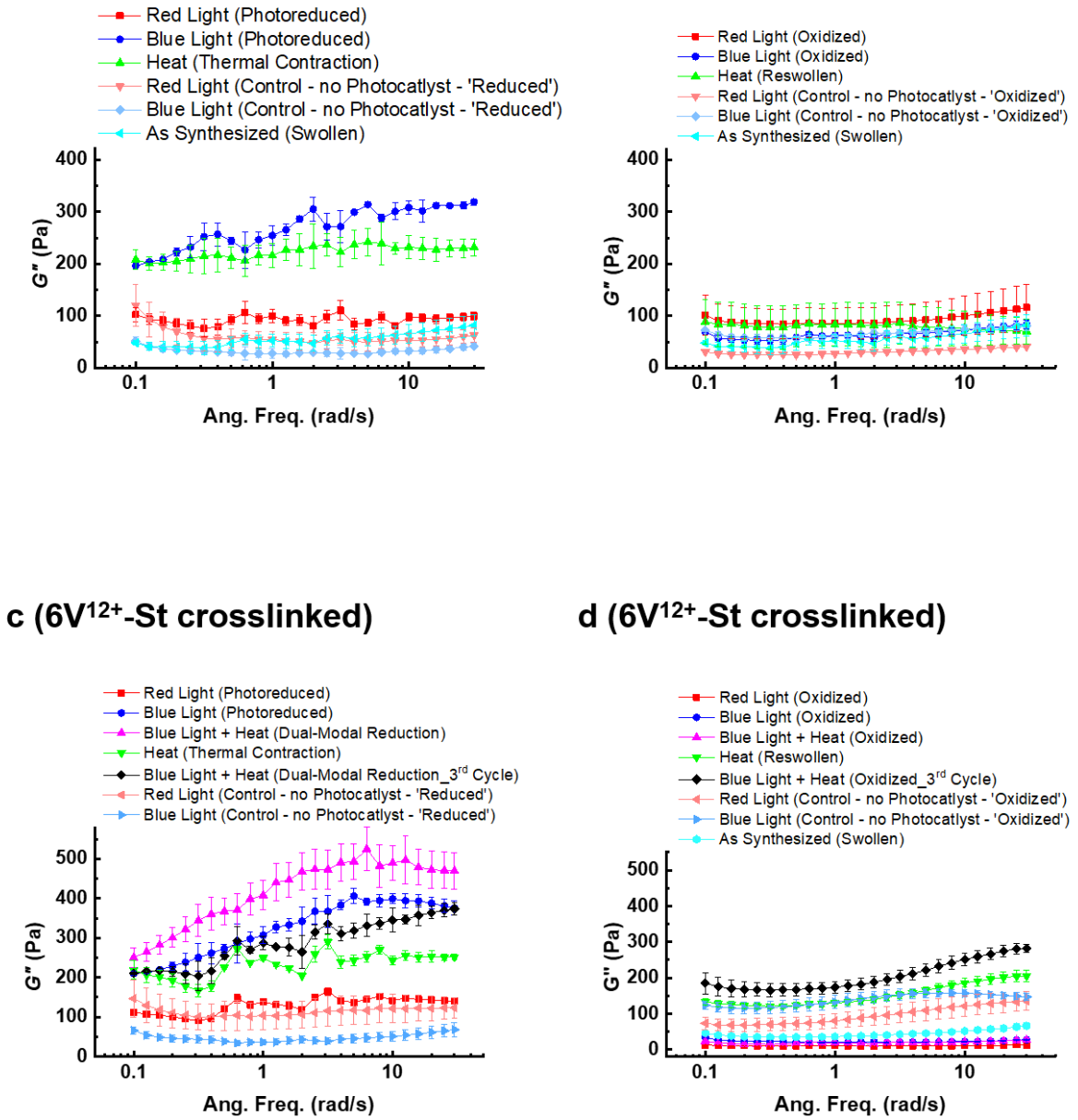


Figure S20: a) Loss modulus (G'') of the photoreduced and thermally-contracted **2V^{4+}-St** crosslinked hydrogels, **b**) Loss modulus (G'') of the oxidized, re-swollen, and as-synthesized (swollen) **2V^{4+}-St** crosslinked hydrogels, **c**) Loss modulus (G'') of the photoreduced and thermally-contracted **6V^{12+}-St** crosslinked hydrogels, **d**) Loss modulus (G'') of the oxidized, re-swollen, and as-synthesized (swollen) **6V^{12+}-St** crosslinked hydrogels.

4) Bimodal Contraction of Gels: Procedure, Kinetics, and Rheology

The gels were prepared as described in Section D1; and were placed in 125 mL bottles and transferred to a N_2-filled glovebox and swollen for an additional 24 h in a degassed solution of 3.00 mM TEOA in H_2O. The average (n = 3) gel volume at t = 0 was 6.60 cm^3 for the **$6V^{12+}$-St** crosslinked gels. The bottles containing the TEOA solution were sealed with rubber septa, taken out of the glovebox and immediately connected to the N_2-line. The bottles were placed in a large H_2O bath at 50 °C. A small rubber septum was placed under each bottle to ensure uniform heating. The gels were simultaneously irradiated with ~450 nm blue light from the left and right for 5 h, maintaining a 5.5 cm distance between the gel and the light source (**Figure S21**) with volume measurements taken at regular intervals (**Figure S18**). After bimodal reduction/contraction, the gels were removed from the light-heat source and a 20 mm diameter disc was punched out of the material. The gel discs were placed into an airtight container and transported for rheological experiments, which were performed to obtain the reduced/contracted rheological data on the gels (**Figure S19** and **S20**). The resulting discs were oxidized and swollen in H_2O for 48 h. A new 20 mm diameter disc was punched out from the resulting reswollen gels and the oxidized rheological data were recorded (**Figure S19** and **S20**).

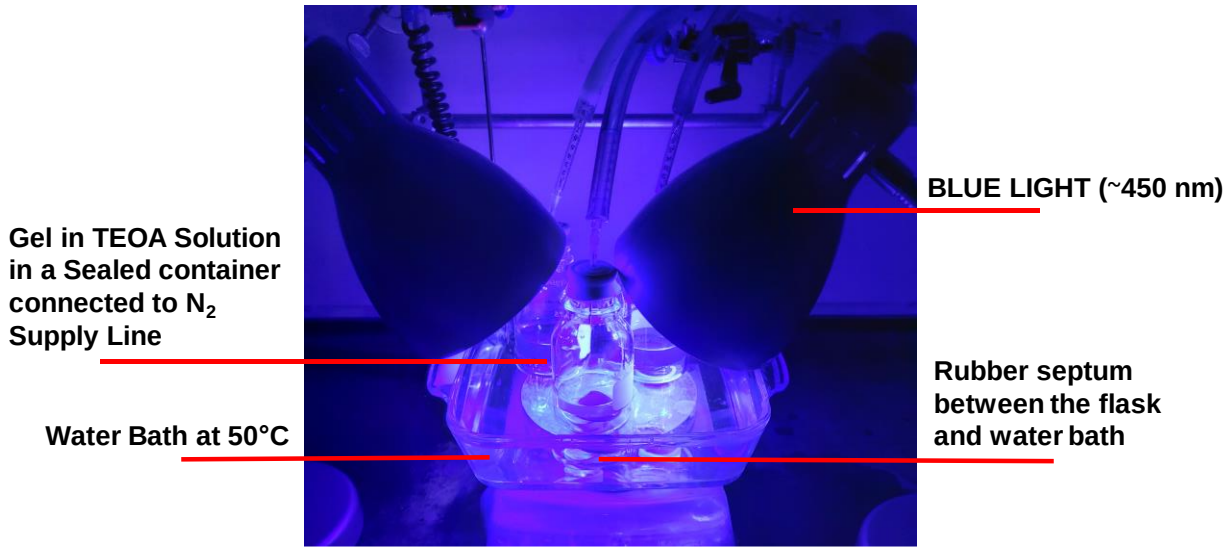


Figure S21: Experimental setup for bimodal redox actuation cycling experiments. Gels in TEOA solution inside sealed 125 mL flasks were heated at 50 °C and irradiated from left and right approximately 5.5 cm away from the gels with ~450 nm blue light source.

5) Bimodal Red-Ox Actuation Cycles (Volume) of $6V^{12+}$-St Gels: Procedure, Kinetics, and Rheology

The gels were prepared as described in Section D1; and were placed in 125 mL bottles and transferred to a N_2-filled glovebox and swollen for an additional 24 h in a degassed solution of 3.00 mM TEOA in H_2O. The average (n = 3) gel volume at t = 0 was 6.92 cm^3 for the **$6V^{12+}$-St** crosslinked gels. The bottles containing the TEOA solution were sealed with rubber septa, taken out of the glovebox and immediately connected to the N_2-line. The bottles were placed in a large H_2O bath at 50°C. A small rubber septum was placed under each bottle to ensure uniform heating. The gels were simultaneously irradiated with ~450 nm blue light from the left and right for 5 h, maintaining a 5.5 cm distance between the gel and the light source (**Figure S21**) with volume measurements taken at the completion of each cycle (**Figure S22**). After bimodal reduction/contraction, the TEOA solution was removed from the gels, which were oxidized by soaking in H_2O for 48 h. The oxidized gels were transferred to the N_2-filled glovebox and swollen for an additional 24 h in a degassed solution of 3.00 mM TEOA in H_2O. This red-ox actuation

process was repeated for a total of three cycles. In the third cycles, the reduced/contracted gels were removed from the light-heat source and a 20 mm diameter disc was punched out of the material. The gel discs were placed into an airtight container and transported for rheological experiments, which were performed to obtain the reduced/contracted rheological data on the gels (**Figure S19** and **S20**). The resulting discs were oxidized and swollen in H_2O. A new 20 mm diameter disc was punched out from the resulting reswollen gels and the oxidized rheological data were recorded (**Figure S19** and **S20**).

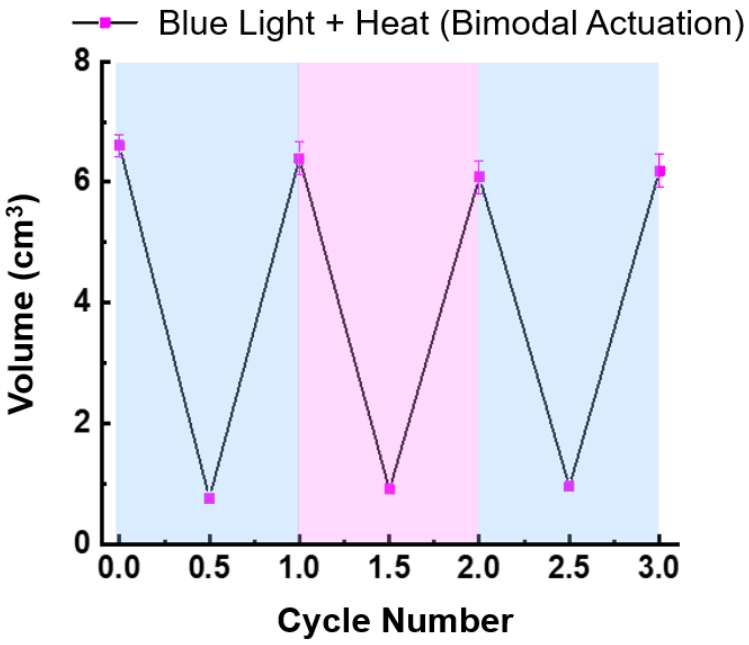


Figure S22: The bimodal redox cycling ability of **6V^{12+}-St** crosslinked hydrogels.

6) Procedure for Quantitative Tensile Testing of Oxidized/Photoreduced $6V^{12+}$-St Crosslinked Hydrogels

All hydrogels used for the tensile experiments were prepared and reduced/contracted by photochemical, thermal, and bimodal processes as described in the Section D1. After reduction/contraction gels were removed from the light, heat, light-heat source and samples shaped like 'dog bones' (2.75 mm wide at their narrowest point and 7.5 mm gage length) were punched out of the material. Each sample was loaded onto the MTS tensile instrument and extended at a rate of 5.0 mm per min until break. The stress (kPa) was measured as a function of strain (%), and Young's modulus was determined using Origin Pro 8 by finding a linear line of best fit for the elastic region of the stress vs. strain curve. The ultimate tensile strength was determined by taking the stress value at the point just before breaking (**Table S2**) (**Figure S23**).

Table S2: Summary of Hydrogel Mechanical Properties

	$6V^{12+}$-St					
Mechanical Properties	Ox	Control (Blue)	Red	Heat	Blue	Blue + Heat
Young's Modulus, *E* (KPa)[a]	14.4 ± 0.4	17.7 ± 1.2	17.9 ± 0.2	23.2 ± 1.8	23.9 ± 2.2	33.0 ± 1.9
Tensile Strength (kPa)[b]	5.5 ± 0.4	13.2 ± 1.2	18.8 ± 0.6	22.8 ± 2.7	28.3 ± 0.7	40.3 ± 3.1
Elongation at Break, ε_B (%)[c]	37.3 ± 1.5	69.7 ± 3.0	103.8 ± 1.3	103.2 ± 4.7	110.7 ± 2.5	116.5 ± 4.7
G′ (Pa)[d]	494	787	1953	3465	4397	4841
G″ (Pa)[d]	36	36	131	237	297	399

[a] Determined from the slope of the linear elastic region of each stress vs strain curve. [b] The tensile strength of each sample was determined from the maximum stress value just before break. [c] Elongation at break was determined from the maximum percent strain when the sample broke. [d] Determined at 10 rad/s.

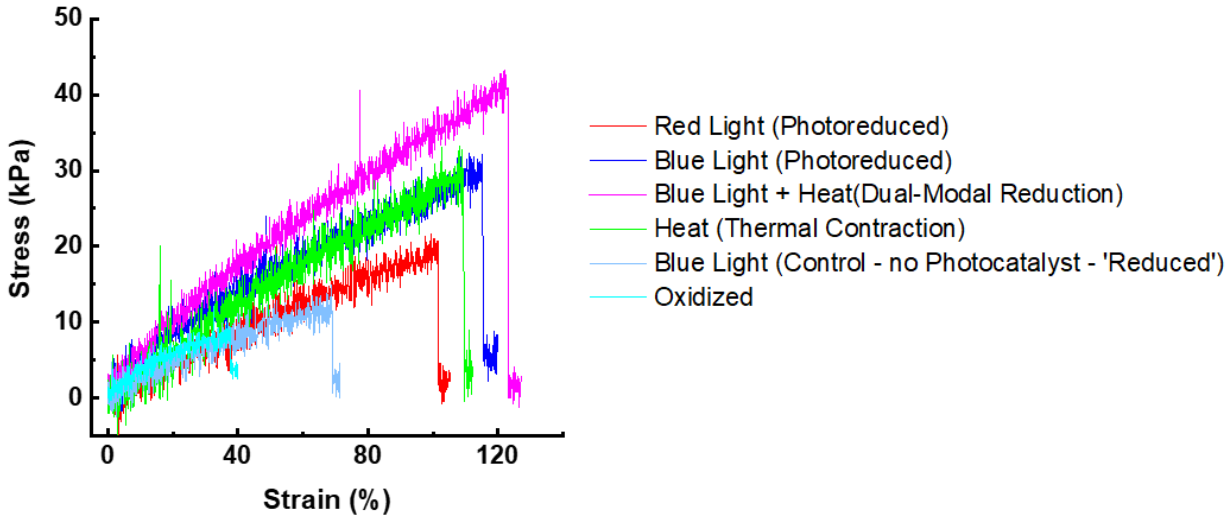


Figure S23: Dynamic tensile testing of hydrogels containing **6V^{12+}-St** crosslinker.

7) Calculations of Crosslinking Density, Swelling Ratio, and M_c

The volumetric swelling ratio[8], Q, was calculated as follows: $Q = 1 + \frac{\rho_{HEA-NIPAM}}{\rho_{H2O}}\left(\frac{M_s}{M_d} - 1\right)$, where $\rho_{HEA\text{-}NIPAM}$ is the density of poly(2-hydroxyethyl acrylate) at 298 K (1.20 g/mL, average calculated data[9, 10]), ρ_{H2O} is the density of H_2O at 298 K (0.997 g/mL) , M_s is the mass of the swollen gel in H_2O, and M_d is the mass of the dried gel. The crosslinking density[11] was calculated as follows: Crosslinking Density = $\frac{G(\sqrt[3]{Q})}{RT}$, where G is the equilibrium shear modulus ($\sqrt{(G')^2 + (G'')^2}$ from oscillatory shear rheology at 1 rad s^{-1} and 1 % strain), R is the gas constant (8.314459848 $\frac{m^3 Pa}{mol\ K}$), and T = 298K, in units of $\frac{mol}{m^3}$. The average molecular weight between crosslinks[12] (M_c) was calculated as follows: $M_c = \frac{\rho_{gel} RT}{G}$ where ρ_{gel} is the density of the gel ((M_d / (M_s–M_d)) * ρ_{H2O}) in $\frac{g}{cm^3}$, R is the gas constant (8.314459848 x 10^6 $\frac{cm^3 Pa}{mol\ K}$), and T = 298 K, in units of $\frac{g}{mol}$.

Table S3: Crosslinking Density, Swelling Ratio, and M_c of **2V^{4+}-St** and **6V^{12+}-St** crosslinked hydrogels

Crosslinker	Q (Swelling Ratio)	G (Pa)	Crosslinking Density (mol/m^3)	M_c (kDa)
2V^{4+}-St	20.352	495	0.978	173
6V^{12+}-St	51.460	886	0.744	119

Section E: References

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