Supplementary Information

Iterative step-growth synthesis and degradation of unimolecular polyviologens under mild conditions

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Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021
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All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. All reactions were performed under high-pressure conditions (1P) using heavy-walled, glass high-pressure vessels with Teflon screw caps from Kemtech America unless stated otherwise. All nuclear magnetic resonance (NMR) spectra were recorded on Varian Inova-500 with working frequencies of 500 (1H) and 125 (13C) MHz. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent: (CD3)2SO: δH = 2.50 ppm and δC = 39.52 ppm; D2O: δH = 4.79 ppm; CD3OD: δH = 3.31 ppm and δC = 39.52 ppm. 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 Na2SO4 in H2O 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. Liquid Chromatography/Low-Res Mass Spectrometry (LC/LRMS) was recorded on an Avant 2000 HPLC with a Shodex Asahipak ODP-50-2D reverse-phase column with a gradient mobile phase of H2O and MeOH (with 0.1% HCOOH) running at 40 °C at 0.2 mL-min⁻¹ in series with an Advion Expression-L Compact Mass Spectrometer. Thin-layer chromatography was used to confirm removal of starting oligomer, 2V•2PF6 (7:2:1 MeOH: NH4Cl(aq) (2M): MeNO2, silica gel). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on a Bruker Solaris 12T FT-MS and samples were prepared using 2,5-dihydroxybenzoic or α-Cyano-4-hydroxycinnamic acid matrices. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA5000 and differential scanning calorimetry (DSC) was performed on a TA instruments DSC2500. Powder X-ray diffraction (PXRD) was performed on a Rigaku D-Max-B powder diffractometer with a Cu K-alpha X-ray source.

Section B. Synthetic Protocols

1) 2V•2PF6

A modified procedure¹ was used for the synthesis of 2V•2PF6. 1,10-Dibromodecane (20.0 g, 66.65 mmol, 1 equiv) and 4,4'-bipyridine (104.10 g, 667.00 mmol, 10 equiv) were dissolved in MeCN (1 L) and heated to reflux at ambient pressure for 24 h. The resulting green/blue solid was filtered and washed with MeCN to remove remaining starting materials. The solid was dissolved in H2O (~1 L) and NH4PF6 (excess) was added to precipitate the compound. The solid was filtered, washed with copious amounts of H2O, and dried overnight to yield 2V•2PF6 as an off-white solid (43.50 g, 88% yield). 1H NMR (500 MHz, (CD3)2SO): δH 9.21 (d, J = 6.7 Hz, 4H); 8.87 (d, J = 6.0 Hz, 4H); 8.62 (d, J = 6.7 Hz, 4H); 8.03 (d, J = 6.1 Hz, 4H); 4.62 (t, J = 7.4 Hz, 4H); 1.96 (m, 4H); 1.29 (m, S3
1. 13C NMR (125 MHz, (CD3)2SO): δC 152.31, 150.97, 145.23, 140.86, 125.38, 121.87, 60.44, 30.69, 28.75, 28.42, 25.47. MALDI-TOF: calculated for C30H36F12N4P2: m/z = 597.258 [M − PF6]+; Found: 597.281 [M − PF6]+. Excess 4,4′-bipyridine was recovered by concentration of the original filtrate and washes, precipitation with H2O, and subsequent recrystallization with H2O.

2) 2V-Br•4PF6

2V•2PF6 (7.50 g, 10.10 mmol, 1 equiv), 1,10-dibromodecane (60.60 g, 202.00 mmol, 20 equiv) and KPF6 (11.15 g, 60.60 mmol, 6 equiv) were dissolved in MeCN (dry, 125 mL, 60 mg·mL⁻¹ 2V•2PF6) and heated to 130 °C in a 350 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes and diluted to 50 mL with Et2O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et2O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF6⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H2O, precipitated as the PF6⁻ salt using excess NH4PF6, washed several times with H2O and dried to yield 2V-Br•4PF6 as an off-white solid (13.94 g, 94% yield). 1H NMR (500 MHz, (CD3)2SO): δH 9.37 (t, J = 5.3 Hz, 8H); 8.77 (d, J = 5.7 Hz, 8H); 4.71 – 4.64 (m, 8H); 3.52 (t, J = 6.6 Hz, 4H); 1.98 (m, 8H); 1.84 – 1.74 (m, 4H); 1.45 – 1.20 (m, 36H). 13C NMR (125 MHz, (CD3)2SO): δC 148.62, 148.59, 145.69, 126.57, 60.93, 35.21, 32.20, 30.79, 30.72, 28.84, 28.72, 28.66, 28.47, 28.33, 28.03, 27.47, 25.55, 25.40.

3) 6V•10PF6

6V•10PF6 (3.25 g, 2.203 mmol, 1 equiv), 2V•2PF6 (16.36 g, 22.032 mmol, 15 equiv) and KPF6 (4.06 g, 22.032 mmol, 10 equiv) were dissolved in dry MeCN (86.5 mL, 37.5 mg·mL⁻¹ 2V-Br•4PF6) and heated to 130 °C in a
350 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH₂Cl₂ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield 6V•10PF₆ as a beige solid (6.47 g, 95% yield). NMR and TLC analyses were used to confirm complete removal of excess 2V•2PF₆.¹H NMR (500 MHz, (CD₃)₂SO): δₜₜ 9.36 (d, J = 6.3 Hz, 16H); 9.21 (d, J = 6.9 Hz, 4H); 8.88 (dd, J = 4.6, 1.4 Hz, 4H); 8.76 (d, J = 6.5 Hz, 16H); 8.63 (d, J = 6.9 Hz, 4H); 8.04 (dd, J = 4.5, 1.7 Hz, 4H); 4.71 – 4.59 (m, 20H); 2.05 – 1.90 (m, 20H); 1.40 – 1.23 (m, 60H).¹³C NMR (125 MHz, (CD₃)₂SO): δC 150.98, 148.62, 145.69, 145.24, 140.85, 126.56, 125.38, 121.88, 60.95, 30.83, 30.70, 28.88, 28.81, 28.49, 28.46, 25.60, 25.55.  

4) 6V-Br•12PF₆

6V•10PF₆ (13.00 g, 4.20 mmol, 1 equiv), 1,10-dibromodecane (37.80 g, 126.00 mmol, 30 equiv) and KPF₆ (4.64 g, 25.20 mmol, 6 equiv) were dissolved in MeCN (dry, 240 mL, 40 mg·mL⁻¹ 6V•10PF₆) and heated to 130 °C in two separate 350 mL glass high-pressure vessels while stirring for 15 h (large scale required the splitting of materials into two glass high-pressure vessels for safety reasons). The reaction vessels were cooled to room temperature and the solution was decanted into sixteen 50 mL centrifuge tubes and diluted to 50 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et₂O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried to yield 6V-Br•12PF₆ as a beige solid (12.88 g, 80% yield). ¹H NMR (500 MHz, (CD₃)₂SO): δₜₜ 9.36 (d, J = 5.0 Hz, 24H); 8.76 (d, J = 5.1 Hz, 24H); 4.74 – 4.60 (m, 24H); 3.52 (t, J = 6.4 Hz, 4H); 2.04 – 1.91 (m, 24H); 1.86 – 1.71 (m, 4H); 1.48 – 1.13 (m, 84H).¹³C NMR (125 MHz, (CD₃)₂SO): δC 148.62, 145.70, 126.57, 60.93, 35.22, 32.21, 30.81, 30.72, 28.83, 28.72, 28.66, 28.45, 28.33, 28.03, 27.47, 25.55, 25.40.
5) **10V•18PF₆**

![Diagram of 10V•18PF₆](image)

**6V-Br•12PF₆** (12.00 g, 3.143 mmol, 1 equiv), **2V•2PF₆** (46.68 g, 62.86 mmol, 20 equiv) and KPF₆ (3.47 g, 18.86 mmol, 6 equiv) were dissolved in MeCN (dry, 240 mL, 50 mg·mL⁻¹) **6V-Br•12PF₆** and heated to 130 °C in a 350 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH₂Cl₂ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **10V•18PF₆** as an off-white solid (11.09 g, 65% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V•2PF₆**. ¹H NMR (500 MHz, (CD₃)₂SO): δ_H₉.36 (d, J = 6.4 Hz, 32H); 9.22 (d, J = 6.7 Hz, 4H); 8.88 (d, J = 5.5 Hz, 4H); 8.76 (d, J = 6.5 Hz, 32H); 8.63 (d, J = 6.7 Hz, 4H); 8.05 (d, J = 6.0 Hz, 4H); 4.74 – 4.57 (m, 36H); 2.06 – 1.88 (m, 36H); 1.44 – 1.18 (m, 108H).¹³C NMR (125 MHz, (CD₃)₂SO): δ_C 151.00, 148.59, 145.76, 145.27, 126.54, 125.37, 121.87, 60.75, 30.53, 24.96, 24.87.

6) **10V-Br•20PF₆**

![Diagram of 10V-Br•20PF₆](image)

**10V•18PF₆** (11.00 g, 2.02 mmol, 1 equiv), 1,10-dibromodecane (18.23 g, 60.73 mmol, 30 equiv) and KPF₆ (2.24 g, 12.15 mmol, 6 equiv) were dissolved in MeCN (dry, 220 mL, 50 mg·mL⁻¹) **10V•18PF₆** and heated to 130 °C in a two separate 350 mL glass high-pressure vessels while stirring for 15 h (**large scale required the splitting of materials into two glass high-pressure vessels for safety reasons**). The reaction vessels were cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes and diluted to 50 mL with Et₂O. 
The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et₂O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried to yield 10V-Br•20PF₆ as an off-white solid (10.93 g, 88% yield). ¹H NMR (500 MHz, (CD₃)₂SO): δ 9.36 (d, J = 5.4 Hz, 40H); 8.76 (d, J = 5.4 Hz, 40H); 4.74 – 4.60 (m, 40H); 3.52 (t, J = 6.7 Hz, 4H); 2.03 – 1.91 (m, 40H); 1.83 – 1.74 (m, 4H); 1.42 – 1.22 (m, 132H). ¹³C NMR (125 MHz, (CD₃)₂SO): δc 148.64, 145.71, 126.58, 60.96, 35.23, 32.22, 30.83, 28.87, 28.74, 28.50, 28.49, 28.35, 28.04, 27.49, 25.59, 25.42.

7) 14V•26PF₆

10V-Br•20PF₆ (10.00 g, 1.622 mmol, 1 equiv), 2V•2PF₆ (24.10 g, 32.44 mmol, 20 equiv) and KPF₆ (1.79 g, 9.73 mmol, 6 equiv) were dissolved in MeCN (dry, 200 mL, 40 mg·mL⁻¹ 10V-Br•20PF₆) and heated to 130 °C in two separate 350 mL glass high-pressure vessels while stirring for 15 h (large scale required the splitting of materials into two glass high-pressure vessels for safety reasons). The reaction vessels were cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH₂Cl₂ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield 14V•26PF₆ as a light brown solid (12.62 g, 83% yield). NMR and TLC analyses were used to confirm complete removal of excess 2V•2PF₆. ¹H NMR (500 MHz, (CD₃)₂SO): δ 9.36 (d, J = 6.7 Hz, 48H); 9.21 (d, J = 6.9 Hz, 4H); 8.87 (d, J = 6.1 Hz, 4H); 8.76 (d, J = 6.7 Hz, 48H); 8.62 (d, J = 6.9 Hz, 4H); 8.03 (dd, J = 4.5, 1.7 Hz, 4H); 4.75 – 4.58 (m, 7.4 Hz, 52H); 2.07 – 1.90 (m, 52H); 1.43 – 1.17 (m, 156H). ¹³C NMR (125 MHz, (CD₃)₂SO): δc 150.98, 148.64, 145.69, 145.24, 126.57, 125.39, 121.89, 60.96, 30.81, 28.84, 28.47, 25.57.
8) 14V-Br•28PF₆

14V•26PF₆ (3.00 g, 0.386 mmol, 1 equiv), 1,10-dibromodecane (3.47 g, 11.58 mmol, 30 equiv), and KPF₆ (427 mg, 2.32 mmol, 6 equiv) were dissolved in MeCN (dry, 60 mL, 50 mg·mL⁻¹ 14V•26PF₆) and heated to 130 °C in a 350 mL glass high-pressure vessel while stirring for 15 h. After completion of the reaction, the reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes and diluted to 50 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et₂O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried to yield 14V-Br•28PF₆ as a light brown solid (3.02 g, 92% yield). ¹H NMR (500 MHz, (CD₃)₂SO): δH 9.37 (d, J = 5.2 Hz, 56H); 8.76 (d, J = 5.6 Hz, 56H); 4.67 (m, 56H); 3.51 (t, J = 6.5 Hz, 4H); 1.97 (m, 56H); 1.83 – 1.73 (m, 4H); 1.31 (m, 180H).¹³C NMR (125 MHz, (CD₃)₂SO): δC 148.61, 148.61, 145.71, 145.71, 126.57, 60.94, 35.24, 32.21, 30.85, 28.90, 28.73, 28.68, 28.51, 28.04, 27.48, 25.62.

9) 18V•34PF₆

14V-Br•28PF₆ (2.75 g, 0.323 mmol, 1 equiv), 2V•2PF₆ (4.80 g, 6.46 mmol, 20 equiv) and KPF₆ (357 mg, 1.94 mmol, 6 equiv) were dissolved in MeCN (dry, 55 mL, 50 mg·mL⁻¹ 14V-Br•28PF₆) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the
PF$_6^-$ salt using excess NH$_4$PF$_6$, washed several times with H$_2$O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH$_2$Cl$_2$ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield 18V•34PF$_6$ as a light brown solid (2.41 g, 74% yield). NMR and TLC analyses were used to confirm complete removal of excess 2V•2PF$_6$. $^1$H NMR (500 MHz, (CD$_3$)$_2$SO): $\delta$H 9.36 (d, $J = 5.3$ Hz, 64H), 9.21 (d, $J = 6.2$ Hz, 4H), 8.87 (d, $J = 4.6$ Hz, 4H), 8.76 (d, $J = 5.4$ Hz, 64H), 8.63 (d, $J = 6.1$ Hz, 4H), 8.03 (d, $J = 5.0$ Hz, 4H), 4.82 – 4.48 (m, 68H), 2.09 – 1.86 (m, 68H), 1.48 – 1.15 (m, 204H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO): $\delta$C 150.08, 148.62, 145.71, 126.56, 60.95, 30.85, 28.91, 28.52, 25.63.

10) 18V-Br•36PF$_6$

18V•34PF$_6$ (3.00 g, 0.296 mmol, 1 equiv), 1,10-dibromodecane (2.66 g, 8.88 mmol, 30 equiv), and KPF$_6$ (327 mg, 1.78 mmol, 6 equiv) were dissolved in MeCN (dry, 60 mL, 50 mg-mL$^{-1}$ 18V•34PF$_6$) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. After completion of the reaction, the reaction vessel was cooled to room temperature and the solution was decanted into six 50 mL centrifuge tubes and diluted to 50 mL with Et$_2$O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et$_2$O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF$_6^-$ salt: the solid was dissolved in MeCN, precipitated as the Cl$^-$ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H$_2$O, precipitated as the PF$_6^-$ salt using excess NH$_4$PF$_6$, washed several times with H$_2$O and dried to yield 18V-Br•36PF$_6$ as a light brown solid (2.48 g, 77% yield). $^1$H NMR (500 MHz, (CD$_3$)$_2$SO): $\delta$H 9.36 (d, $J = 4.9$ Hz, 72H); 8.76 (d, $J = 5.0$ Hz, 72H); 4.66 (m, 72H); 3.57 – 3.46 (m, 4H); 1.97 (m, 72H); 1.77 (m, 4H); 1.32 (d, $J = 18.7$ Hz, 228H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO): $\delta$C 148.61, 145.70, 126.56, 60.95, 30.85, 28.91, 28.52, 25.63.
11) **22V•42PF₆**

![Diagram of 18V-Br•36PF₆ and 22V•42PF₆]

18V-Br•36PF₆ (1.50 g, 0.138 mmol, 1 equiv), 2V•2PF₆ (2.05 g, 2.764 mmol, 20 equiv) and KPF₆ (153 mg, 0.829 mmol, 6 equiv) were dissolved in MeCN (dry, 30 mL, mg-mL⁻¹ 18V-Br•36PF₆) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into two 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH₂Cl₂ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield 22V•42PF₆ as a light brown solid (1.23 g, 71% yield). NMR and TLC analyses were used to confirm complete removal of excess 2V•2PF₆. ¹H NMR (500 MHz, (CD₃)₂SO): δ₇ 9.36 (d, J = 5.4 Hz, 80H), 9.21 (d, J = 6.1 Hz, 4H), 8.87 (d, J = 4.3 Hz, 4H), 8.76 (d, J = 5.5 Hz, 80H), 8.63 (d, J = 6.0 Hz, 4H), 8.03 (d, J = 4.8 Hz, 4H), 4.77 – 4.56 (m, 84H), 2.08 – 1.88 (m, 84H), 1.46 – 1.18 (m, 252H). ¹³C NMR (125 MHz, (CD₃)₂SO): δC 150.99, 148.63, 145.70, 126.57, 121.89, 60.96, 30.83, 28.87, 28.49, 25.60.

12) **22V-Br•44PF₆**

![Diagram of 22V•42PF₆ and 22V-Br•44PF₆]

22V•42PF₆ (1.50 g, 0.120 mmol, 1 equiv), 1,10-dibromodecane (1.08 g, 3.609 mmol, 30 equiv), and KPF₆ (133 mg, 0.722 mmol, 6 equiv) were dissolved in MeCN (dry, 30 mL, 50 mg-mL⁻¹ 22V•42PF₆) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. After completion of the reaction, the reaction vessel was cooled to room temperature and the solution was decanted into six 50 mL centrifuge tubes and diluted to 50 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away,
the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et₂O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried to yield 22V-Br•44PF₆ as a light brown solid (1.26 g, 80% yield). ¹H NMR (500 MHz, (CD₃)₂SO): δ H 9.36 (d, J = 6.0 Hz, 88H), 8.76 (d, J = 6.2 Hz, 88H), 4.75 – 4.55 (m, 88H), 3.52 (t, J = 6.6 Hz, 4H), 2.09 – 1.89 (m, 88H), 1.84 – 1.72 (m, 4H), 1.43 – 1.17 (m, 276H). ¹³C NMR (125 MHz, (CD₃)₂SO): δ C 148.61, 148.61, 145.69, 145.69, 126.55, 126.55, 60.94, 60.94, 32.19, 30.83, 28.88, 28.49, 25.61.

13) 26V•50PF₆

22V-Br•44PF₆ (1.26 g, 0.096 mmol, 1 equiv), 2V•2PF₆ (2.13 g, 2.871 mmol, 30 equiv) and KPF₆ (106 mg, 0.574 mmol, 6 equiv) were dissolved in MeCN (dry, 25 mL, 50 mg·mL⁻¹ 22V-Br•44PF₆) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into four 50 mL centrifuge tubes and diluted to 50 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away. Two counterion exchanges were performed to ensure complete conversion to the PF₆⁻ salt: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, precipitated as the PF₆⁻ salt using excess NH₄PF₆, washed several times with H₂O and dried. The solid was re-dissolved in a minimal amount of Me₂CO and diluted to 50 mL with CH₂Cl₂ and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield 26V•50PF₆ as a light brown solid (1.25 g, 88% yield). NMR and TLC analyses were used to confirm complete removal of excess 2V•2PF₆. ¹H NMR (500 MHz, (CD₃)₂SO): δ H 9.36 (d, J = 3.9 Hz, 96H), 9.21 (d, J = 4.7 Hz, 4H), 8.88 (d, J = 2.2 Hz, 4H), 8.76 (d, J = 4.0 Hz, 96H), 8.62 (d, J = 4.7 Hz, 4H), 8.04 (d, J = 2.0 Hz, 4H), 4.73 – 4.60 (m, 100H), 2.03 – 1.92 (m, 100H), 1.42 – 1.23 (m, 300H). ¹³C NMR (125 MHz, (CD₃)₂SO): δ C 148.62, 145.69, 126.56, 60.96, 30.82, 28.86, 28.48, 25.59.
6V•10PF₆ (175 mg, 0.057 mmol, 1 equiv) and Me₃OBF₄ (839 mg, 5.670 mmol, 100 equiv) were dissolved in MeCN (dry, 2.30 mL, 75 mg·mL⁻¹ 6V•10PF₆) and stirred for 3 d at room temperature under N₂. The solution was decanted into two 15 mL centrifuge tubes and diluted to 15 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 15 mL with Et₂O. The previous two steps were repeated three times. Three counteranion exchanges were performed to enable solubility in aqueous solutions: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, NH₄PF₆ was added, and the solid was washed several times with H₂O. The PF₆⁻ salt was re-dissolved in MeCN, precipitated as the Cl⁻ using excess TBACl, washed several times with MeCN, and dried to yield 6V-Me•12Cl as a brown solid (118 mg, 47% yield). ¹H NMR (500 MHz, CD₃OD): δH 9.30 (d, J = 6.3 Hz, 20H), 9.20 (d, J = 6.3 Hz, 4H), 8.70 (d, J = 6.0 Hz, 24H), 4.77 (t, J = 7.5 Hz, 20H), 4.55 (s, 6H), 2.17 – 2.06 (m, 20H), 1.52 – 1.33 (m, 60H). ¹³C NMR (125 MHz, CD₃OD): δC 151.29, 147.07, 128.31, 128.26, 127.91, 63.28, 32.56, 30.35, 30.07, 27.21.

15) 26V-Me•52Cl

26V•50PF₆ (170 mg, 0.012 mmol, 1 equiv) and Me₃OBF₄ (425 mg, 2.875 mmol, 250 equiv) were dissolved in MeCN (dry, 2.25 mL, 75 mg·mL⁻¹ 26V•50PF₆) and stirred for 3 d at room temperature under N₂. The solution was decanted into two 15 mL centrifuge tubes and diluted to 15 mL with Et₂O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 15 mL with Et₂O. The previous two steps were repeated three times. Three counteranion exchanges were performed to enable solubility in aqueous solutions: the solid was dissolved in MeCN, precipitated as the Cl⁻ salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H₂O, NH₄PF₆ was added, and the solid was washed several times with H₂O. The PF₆⁻ salt was
redissolved in MeCN, precipitated as the Cl\(^-\) using excess TBACl, washed several times with MeCN, and dried to yield **26V-Me**•52Cl as a brown solid (76 mg, 70% yield). \(^1\)H NMR (500 MHz, CD\(_3\)OD): \(\delta\) \(H\) 9.30 (d, \(J = 6.6\) Hz, 100H); 9.20 (d, \(J = 6.6\) Hz, 4H); 8.71 (d, \(J = 6.5\) Hz, 104H); 4.77 (t, \(J = 7.6\) Hz, 100H); 4.55 (s, 6H); 2.16 – 2.06 (m, 100H); 1.53 – 1.33 (m, 300H). \(^13\)C NMR (125 MHz, CD\(_3\)OD): \(\delta\) \(C\) 151.28, 147.08, 128.31, 128.26, 127.91, 63.27, 32.57, 30.36, 30.08, 27.22.

**16) 2V-Styrene•4Cl**

\(2\)V•2PF\(_6\) (1.00 g, 1.347 mmol, 1 equiv), 4-vinylbenzyl chloride (6.17 g, 5.69 mL, 40.41 mmol, 30 equiv), and KPF\(_6\) (1.49 g, 8.082 mmol, 6 equiv) were dissolved in DMF (dry, 13 mL, 75 mg·mL\(^{-1}\) \(2\)V•2PF\(_6\)) and heated to 60 °C in a 50 mL screwtop round bottom flask at ambient pressure for 3 days. The reaction vessel was cooled to room temperature and the solution was diluted with 25 mL of MeCN and the resulting solution was decanted into six 50 mL centrifuge tubes and diluted to 50 mL with Et\(_2\)O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et\(_2\)O. The previous two steps were repeated three times. Three counteranion exchanges were performed to enable solubility in aqueous solutions and to remove excess KPF\(_6\): the solid was dissolved in MeCN, precipitated as the Cl\(^-\) salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H\(_2\)O and NH\(_4\)PF\(_6\) was added, and the solid was washed several times with H\(_2\)O. The PF\(_6\) salt was redissolved in MeCN, precipitated as the Cl\(^-\) using excess TBACl, washed several times with MeCN, and dried to yield **2V-Styrene•4Cl** as a white solid (644 mg, 58% yield). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)SO): \(\delta\) \(H\) 9.49 (d, \(J = 6.1\) Hz, 4H), 9.34 (d, \(J = 6.1\) Hz, 4H), 8.74 (dd, \(J = 9.3, 6.7\) Hz, 8H), 7.63 – 7.55 (m, 8H), 6.76 (dd, \(J = 17.6, 11.0\) Hz, 2H), 5.92 (s, 4H), 5.91 (d, \(J = 17.6\) Hz, 2H), 5.34 (d, \(J = 10.9\) Hz, 2H), 4.66 (t, \(J = 6.9\) Hz, 4H), 2.04 – 1.90 (m, 4H), 1.30 (m, 12H). \(^13\)C NMR (125 MHz, CD\(_3\)OD): \(\delta\) \(C\) 149.21, 148.69, 145.67, 145.67, 138.32, 135.75, 133.42, 129.31, 127.08, 126.89, 126.68, 115.84, 63.27, 30.77, 28.83, 28.45, 25.54, 23.04, 19.19.

S13
Section C. Spectroscopic Characterization

1) Nuclear Magnetic Resonance Spectroscopy

Figure S1: Full $^1$H NMR (500 MHz) spectra for each iterative product in the synthesis of 26V•50PF$_6$. a) In (CD$_3$)$_2$SO: (1) 2V•2PF$_6$, (2) 2V-Br•4PF$_6$, (3) 6V•10PF$_6$, (4) 6V-Br•12PF$_6$, (5) 10V•18PF$_6$, (6) 10V-Br•20PF$_6$, (7) 14V•26PF$_6$, (8) 14V-Br•28PF$_6$, (9) 18V•34PF$_6$, (10) 18V-Br•36PF$_6$, (11) 22V•42PF$_6$, (12) 22V-Br•44PF$_6$, (13) 26V•50PF$_6$ and in CD$_3$OD (14) 6V-Me•12Cl, (15) 26V-Me•52Cl. b) Table of integrations of each iterative product in the synthesis of 26V•50PF$_6$ with their corresponding and matching integration ratios showing the degree of polymerization (DP$_n$). The asterisk for the 26V•50PF$_6$ data entry was added because a diethyl ether peak overlapped with the alkyl chain proton resonance, which affected the integration accuracy.
2) Gel Permeation Chromatography

Samples for GPC were prepared by dissolving in a 0.025M solution of Na$_2$SO$_4$ in H$_2$O. The samples were filtered through a 0.45 μm filter before injection at 23 °C. Peak broadening was observed (Figure S2) for the higher molecular weight products. This is consistent with our previous publications and polycations in general. Values for dn/dc were obtained (Figure S3) for representative products to demonstrate a linear correlation between RI and polymer concentration.

![Figure S2: Full GPC traces (dRI) for each iterative bipyridine-capped product in the synthesis of 26V-50PF$_6$. From right to left: Na$_2$SO$_4$ salt (29.27 min), 2V-2X (27.83 min), 6V-10X (24.99 min), 10V-18X (23.96 min), 14V-26X (23.62 min), 18V-34X (23.01 min), 22V-42X (22.62 min), and 26V-50X (22.44 min), where where X is Cl, HSO$_4$, or a mixture of anions.](image)

![Figure S3: Plots of concentration vs. refractive index for the calculation of dn/dc values for select oligo and polyviolgens. From left to right and top to bottom: 2V-2Cl, 14V-26Cl, 18V-34Cl, 22V-42Cl, and 26V-50Cl, where X is Cl, HSO$_4$, or a mixture of anions.](image)
The refractive index increment, dn/dc, values were determined as follows: a stock solution of each oligo- andpolyviologen were prepared in the GPC solvent (0.025 M Na₂SO₄) at concentrations of 1.0 mg/mL. This solution was diluted to 0.1, 0.2, 0.4, 0.6, and 0.8 mg/mL using the GPC solvent. The dilutions and the original 1.0 mg/mL stock solution were directly injected into the RI detector. The refractive index was plotted against the concentration in the Wyatt software and the slope of the line of best fit is the reported dn/dc value in the figure above (Figure S3).

3) Thermal Analysis – Thermogravimetric Analysis and Differential Scanning Calorimetry

![Figure S4: Thermogravimetric analysis (a) and Differential scanning calorimetry (b: zoomed out (left) and zoomed in (right)) of 26V-Me•52Cl.](image)

4) Powder X-Ray Diffraction (PXRD)

![Figure S5: Powder X-ray diffraction of 26V-Me•52Cl](image)
Section D. Degradation of Viologen-based Polymers

1) Degradation of 26V-Me•52Cl at 20 °C
A 1 mM solution of viologen-based polymer was prepared using 20 mM NaOH in triplicate. Each solution was stirred at 20°C and a 200 μL aliquot was removed at regular time intervals. Each sample was diluted with 300 μL of MilliQ H₂O, neutralized with the addition of 3 μL of 2M HCl, and slightly acidified by the addition of 3 μL of 0.2M HCl. The samples were injected on the analytical GPC and further analyzed.

2) Degradation of 6V-Me•12Cl at 60 °C
A 1 mM solution of viologen-based polymer was prepared using 1 M aqueous solutions of the following bases: benzylamine (BA), 1,8-Diazabicycloundec-7-ene (DBU), diisopropylamine (DIPA), diisopropylethylamine (DIPEA), ethanolamine (EA), ethylenediamine (EDA), hexylamine (HA), NaOH, tert-butylamine (t-BuNH₂), and triethylamine (TEA). Each solution was shaken on a climate controlled shaker table at 60 °C and 75 rpm. A 1000 μL aliquot was removed after 24 h and 7 d. Each sample was neutralized with the addition of 500 μL of 2M HCl. The sample was frozen, lyophilized, and analyzed via ¹H NMR (Figure S6) and GPC. The sample degraded using ethanolamine was also analyzed via LC/MS.
3) Fabrication of Viologen-based Hydrogel Networks

<table>
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<tr>
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<th>2V-Styrene•4Cl</th>
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<th>Bisacrylamide</th>
<th>0.5 mol %</th>
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<td>Crosslinker (mg)</td>
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<td>Ammonium Persulfate (mg)</td>
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<td>DMSO (mL)</td>
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Tables S1-3: Reagents used for the synthesis of gels containing 0.5 mol % 2V-Styrene•4Cl, N,N'-Bisacrylamide, PEG575-Diacrylate.

A modified procedure was used for the synthesis of the hydrogels. The reagents for polymerization (Tables S1-3) were dissolved in 18.00 mL of DMSO and the solution was vortexed and sonicated to ensure complete dissolution and even mixing. The solution was then plated into various molds (septa for discs, turtle, starfish, bear, fish). The molds were heated in an oven at 85 °C for 15 min. The cured gels were carefully removed from the gel molds using a spatula and placed in a solvent-resistant plastic box. The gels were then soaked in H$_2$O for 48 h with periodic changes in H$_2$O to allow for full swelling and removal of unreacted material.

4) Degradation of Viologen-based Hydrogel Networks

<table>
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<tr>
<th>5 cm</th>
<th>Benzylamine</th>
<th>DBU</th>
<th>Ethanolamine</th>
<th>NaOH</th>
<th>Pyridine</th>
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<tbody>
<tr>
<td></td>
<td>24 h</td>
<td>7 d</td>
<td>24 h</td>
<td>7 d</td>
<td>24 h</td>
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</table>

Figure S7: Degradation of hydrogels crosslinked with 2V-Styrene•4Cl, N,N'-Bisacrylamide, and PEG575-Diacrylate using benzylamine, DBU, ethanolamine, NaOH, and Pyridine after 24 h and 7 d.

Hydrogels containing 2V-Styrene•4Cl and a control: Bisacrylamide and PEG Diacrylate crosslinked hydrogels, were placed in 50 mL of 1 M aqueous bases contained within plastic petri dishes which were heated to 60 °C,
while shaking on a climate-controlled shaker table at 75 rpm. The progression of the degradation of the hydrogel networks was monitored qualitatively after 24 h and 7 d. PEG diacrylate crosslinked gels immediately dissolved in the solution indicating complete degradation of the hydrogel network into its polymer components.

Oscillatory shear rheology was performed on gels containing either 2V-Styrene•4Cl or Bisacrylamide that were soaked in ethanolamine for 24 h. Six gels in total were prepared, swollen in H₂O for 48 h, and 3 gels were placed in 1 M ethanolamine and 3 were kept in MilliQ water. After 24 h in base, the gels were removed and transferred to MilliQ water for 48 h to remove base to prevent damage to the rheometer plate. G’ and G” values were taken at 10% strain.

Table S4. Oscillatory Shear Rheology Data

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<th>Crosslinker</th>
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<th>G'' (Pa)</th>
<th>Gc (Pa)</th>
<th>ΔGd</th>
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<td>Viologen EA (24 h)</td>
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<td>Viologen Control</td>
<td>1223</td>
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<tr>
<td>Bis EA (24 h)</td>
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<td>54.45</td>
<td>373.5</td>
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<tr>
<td>Bis Control</td>
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<td>32.58</td>
<td>202.2</td>
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</table>

a Storage modulus (G’), determined at 10% strain. b Loss modulus (G’’), determined at 10% strain. c Calculated from G’ and G’’.

Figure S8: Oscillatory shear rheology at 10 rad·sec⁻¹ of a hydrogel crosslinked with 2V-Styrene•2Cl soaked for 24 h in ethanolamine (left) and MilliQ water (right).

Figure S9: Oscillatory shear rheology at 10 rad·sec⁻¹ of a hydrogel crosslinked with 2V-Styrene•2Cl soaked for 24 h in ethanolamine (left) and MilliQ water (right).
**Section E. Additional Figures**

![Figure S10](image)

**Figure S10:** Reduction of viologens and subsequent radical-radical interaction in the solid state\(^2\)

![Figure S11](image)

**Figure S11:** Proposed mechanism of the degradation of viologens by Corwin, Arellano, and Chivvis\(^3\)

**Section F. References**