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Supplementary Information

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

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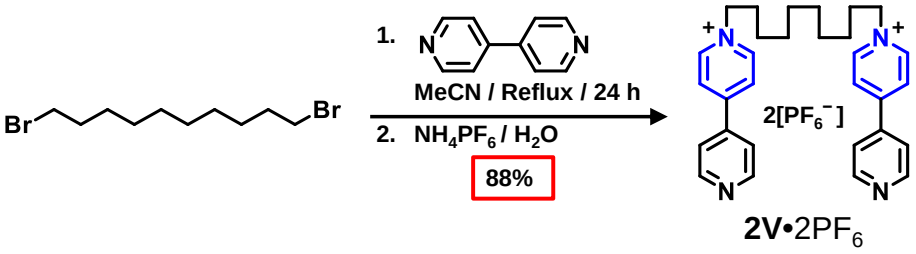
Section A. Materials / General Methods / Instrumentation

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. All reactions were performed under high-pressure conditions (↑P) 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 (^{1}H) and 125 (^{13}C) MHz. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent: $(CD_3)_2SO$: δ_H = 2.50 ppm and δ_C = 39.52 ppm; D_2O: δ_H = 4.79 ppm; CD_3OD: δ_H = 3.31 ppm and δ_C = 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 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. 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 H_2O 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•**$2PF_6$ (7:2:1 MeOH: NH_4Cl(aq) (2M): $MeNO_2$, 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

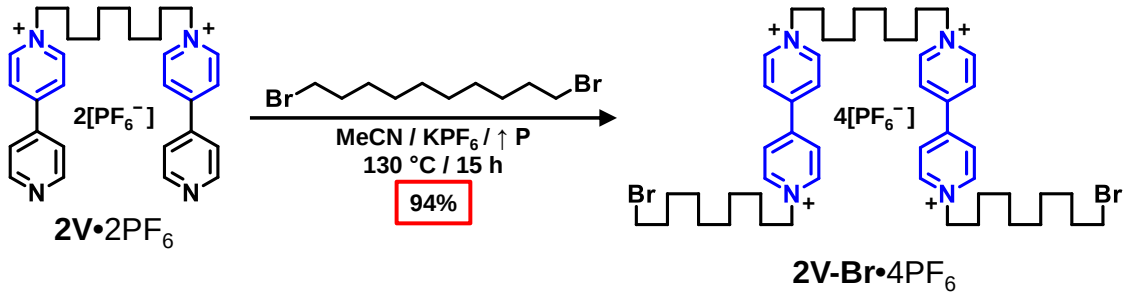
1) 2V•2PF$_6$



A modified procedure[1] was used for the synthesis of **2V•**$2PF_6$. 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 H_2O (~1 L) and NH_4PF_6 (excess) was added to precipitate the compound. The solid was filtered, washed with copious amounts of H_2O, and dried overnight to yield **2V•**$2PF_6$ as an off-white solid (43.50 g, 88% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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,

12H).[13]C NMR (125 MHz, $(CD_3)_2SO$): δ_C 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 $C_{30}H_{36}F_{12}N_4P_2$: *m/z* = 597.258 $[M - PF_6]^+$; Found: 597.281 $[M - PF_6]^+$. Excess 4,4'-bipyridine was recovered by concentration of the original filtrate and washes, precipitation with H_2O, and subsequent recrystallization with H_2O.

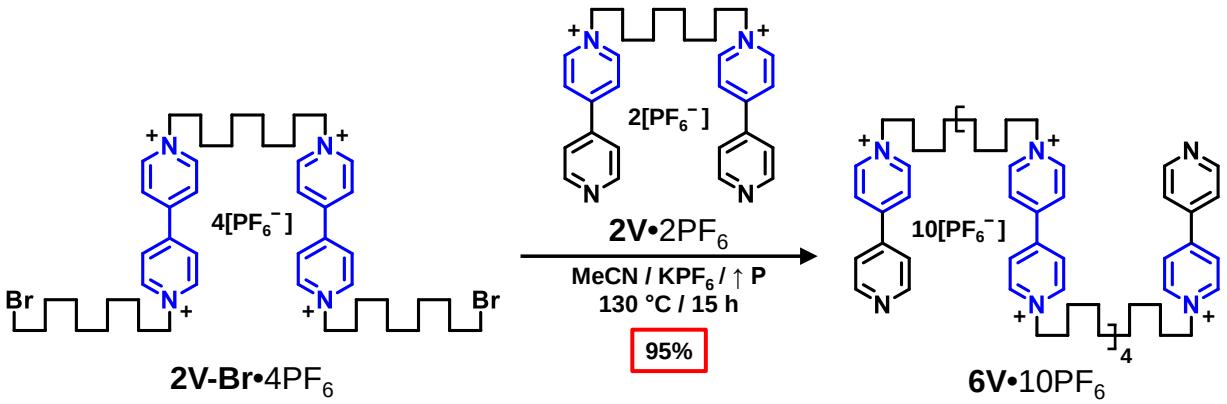
2) 2V-Br•4PF$_6$



2V•2PF$_6$ **2V**•2PF$_6$ **2V-Br**•4PF$_6$

2V•2PF$_6$ (7.50 g, 10.10 mmol, 1 equiv), 1,10-dibromodecane (60.60 g, 202.00 mmol, 20 equiv) and KPF_6 (11.15 g, 60.60 mmol, 6 equiv) were dissolved in MeCN (dry, 125 mL, 60 mg·mL^{-1} **2V**•2PF$_6$) 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 Et_2O. 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_2O. 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried to yield **2V-Br**•4PF$_6$ as an off-white solid (13.94 g, 94% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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).[13]C NMR (125 MHz, $(CD_3)_2SO$): δ_C 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•10PF$_6$

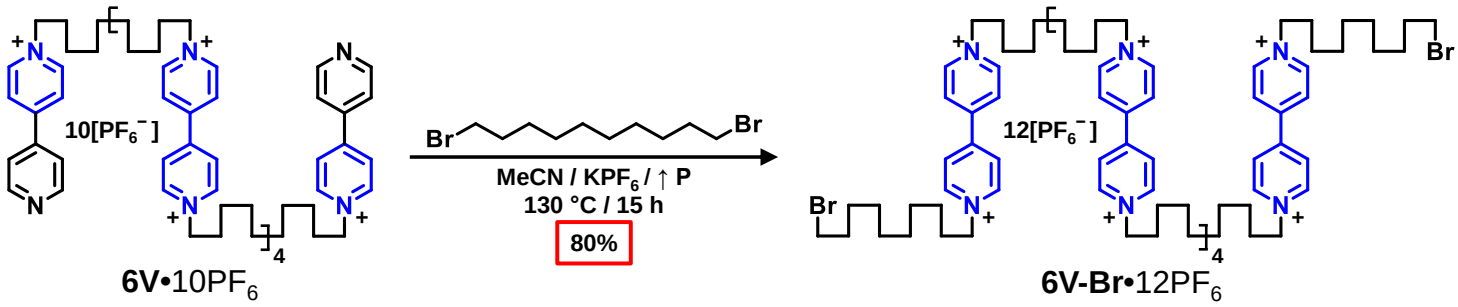


2V-Br•4PF$_6$ **2V**•2PF$_6$ **6V**•10PF$_6$

2V-Br•4PF$_6$ (3.25 g, 2.203 mmol, 1 equiv), **2V**•2PF$_6$ (16.36 g, 22.032 mmol, 15 equiv) and KPF_6 (4.06 g, 22.032 mmol, 10 equiv) were dissolved in dry MeCN (86.5 mL, 37.5 mg·mL^{-1} **2V-Br**•4PF$_6$) and heated to 130 °C in a

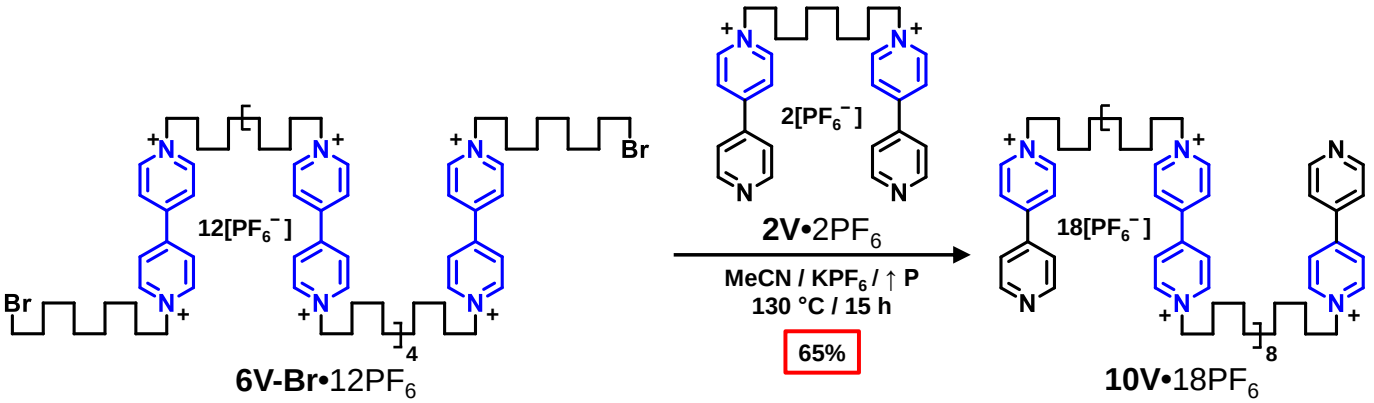
350 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into eight 50 mL centrifuge tubes. Two counterion exchanges were performed to ensure complete conversion to the PF_6 salt: the solid was dissolved in MeCN, precipitated as the Cl^- salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **6V**•$10PF_6$ as a beige solid (6.47g, 95% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V**•$2PF_6$.^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H. 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).^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 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•12PF$_6$



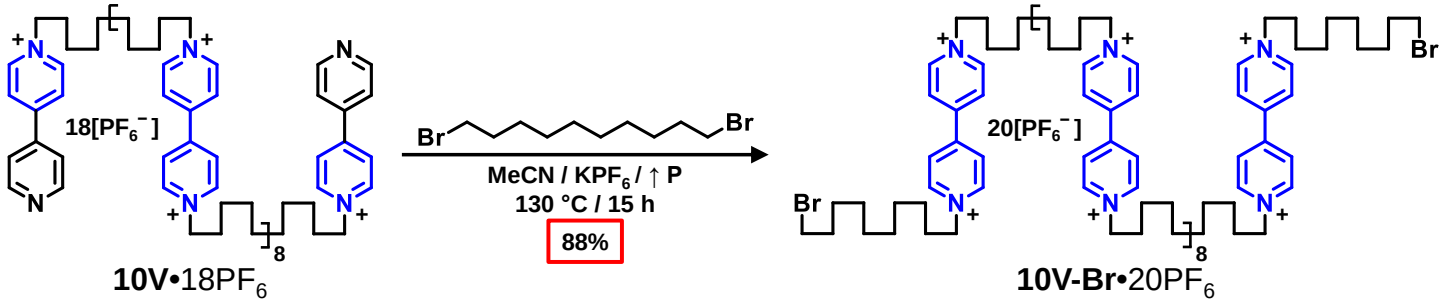
6V•$10PF_6$ (13.00 g, 4.20 mmol, 1 equiv), 1,10-dibromodecane (37.80 g, 126.00 mmol, 30 equiv) and KPF_6 (4.64 g, 25.20 mmol, 6 equiv) were dissolved in MeCN (dry, 240 mL, 40 mg·mL^{-1} **6V**•$10PF_6$) and heated to 130 °C in two separate 350 mL glass high-pressure vessels while stirring for 15 h (*large 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 Et_2O. 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_2O. 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried to yield **6V-Br**•$12PF_6$ as a beige solid (12.88 g, 80% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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).^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 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•18PF$_6$



6V-Br•12PF$_6$ (12.00 g, 3.143 mmol, 1 equiv), **2V**•2PF$_6$ (46.68 g, 62.86 mmol, 20 equiv) and KPF$_6$ (3.47 g, 18.86 mmol, 6 equiv) were dissolved in MeCN (dry, 240 mL, 50 mg·mL^{-1} **6V-Br**•12PF$_6$) 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 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_2O, precipitated as the PF$_6^-$ salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **10V**•18PF$_6$ as an off-white solid (11.09 g, 65% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V**•2PF$_6$. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H. 9.36 (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).^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 151.00, 148.59, 145.76, 145.27, 126.54, 125.37, 121.87, 60.75, 30.53, 24.96, 24.87.

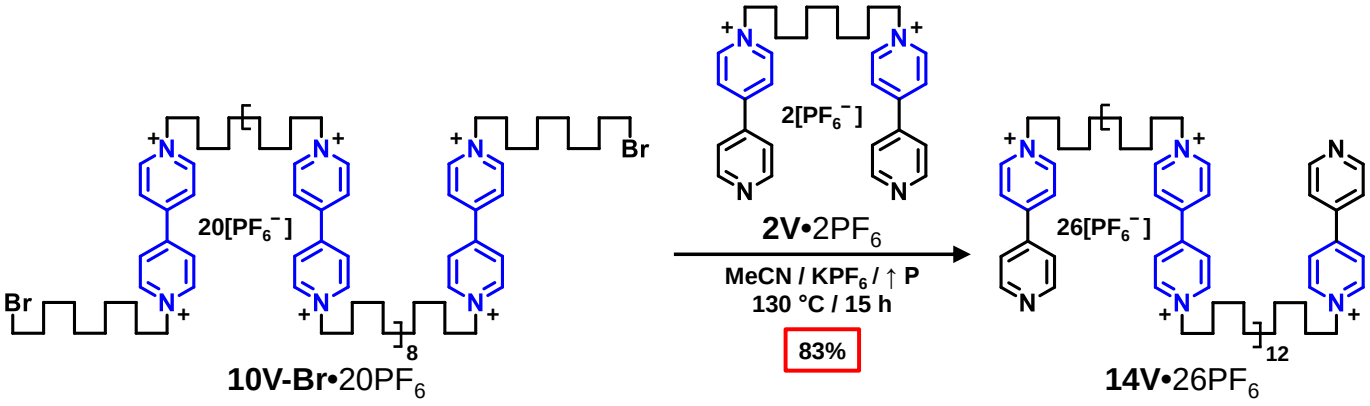
6) 10V-Br•20PF$_6$



10V•18PF$_6$ (11.00 g, 2.02 mmol, 1 equiv), 1,10-dibromodecane (18.23 g, 60.73 mmol, 30 equiv) and KPF$_6$ (2.24 g, 12.15 mmol, 6 equiv) were dissolved in MeCN (dry, 220 mL, 50 mg·mL^{-1} **10V**•18PF$_6$) 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 Et_2O.

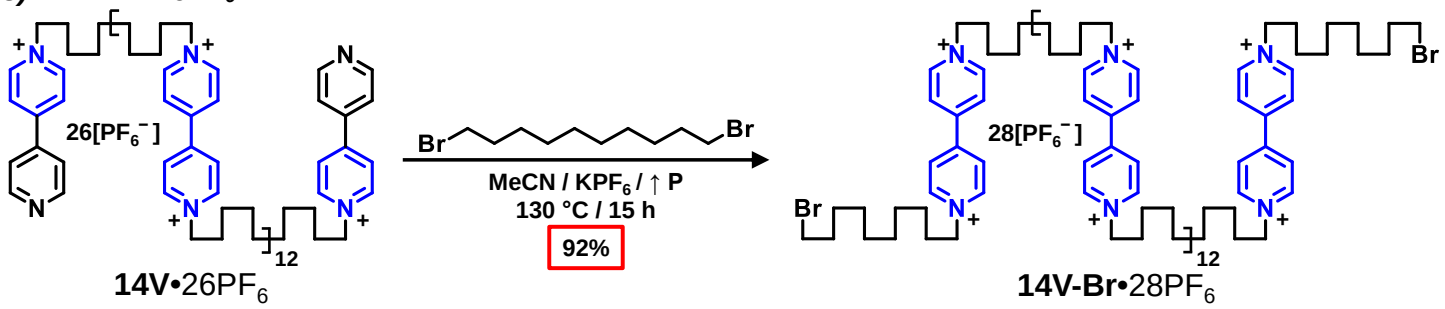
The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away, the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et_2O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF_6 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried to yield **10V-Br•**$20PF_6$ as an off-white solid (10.93 g, 88% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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); 2.04 – 1.91 (m, 40H); 1.83 – 1.74 (m, 4H); 1.42 – 1.22 (m, 132H).^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 148.64, 145.71, 126.58, 60.96, 35.23, 32.22, 30.83, 28.87, 28.74, 28.68, 28.49, 28.35, 28.04, 27.49, 25.59, 25.42.

7) 14V•26PF$_6$



10V-Br•$20PF_6$ (10.00 g, 1.622 mmol, 1 equiv), **2V•**$2PF_6$ (24.10 g, 32.44 mmol, 20 equiv) and KPF_6 (1.79 g, 9.73 mmol, 6 equiv) were dissolved in MeCN (dry, 200 mL, 40 mg·mL^{-1} **10V-Br•**$20PF_6$) 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 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **14V•**$26PF_6$ as a light brown solid (12.62 g, 83% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V•**$2PF_6$. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H. 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).^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 150.98, 148.64, 145.69, 145.24, 126.57, 125.39, 121.89, 60.96, 30.81, 28.84, 28.47, 25.57.

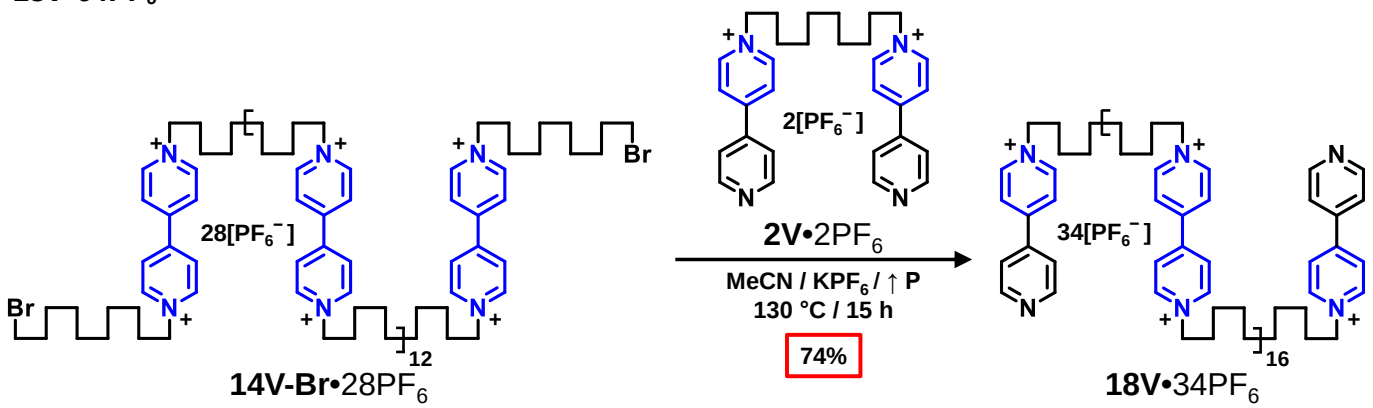
8) 14V-Br•28PF$_6$



14V•26PF$_6$ **14V-Br**•28PF$_6$

14V•26PF$_6$ (3.00 g, 0.386 mmol, 1 equiv), 1,10-dibromodecane (3.47 g, 11.58 mmol, 30 equiv), and KPF$_6$ (427 mg, 2.32 mmol, 6 equiv) were dissolved in MeCN (dry, 60 mL, 50 mg·mL^{-1} **14V**•26PF$_6$) 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 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 **14V-Br**•28PF$_6$ as a light brown solid (3.02 g, 92% yield). ^{1}H NMR (500 MHz, (CD$_3$)$_2$SO): δ_H 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).^{13}C NMR (125 MHz, (CD$_3$)$_2$SO): δ_C 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•34PF$_6$

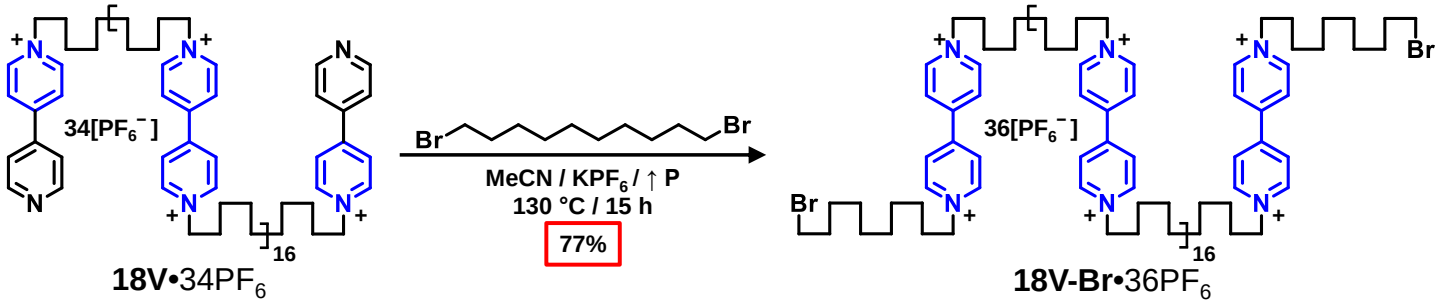


14V-Br•28PF$_6$ **18V**•34PF$_6$

14V-Br•28PF$_6$ (2.75 g, 0.323 mmol, 1 equiv), **2V**•2PF$_6$ (4.80 g, 6.46 mmol, 20 equiv) and KPF$_6$ (357 mg, 1.94 mmol, 6 equiv) were dissolved in MeCN (dry, 55 mL, 50 mg·mL^{-1} **14V-Br**•28PF$_6$) 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 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

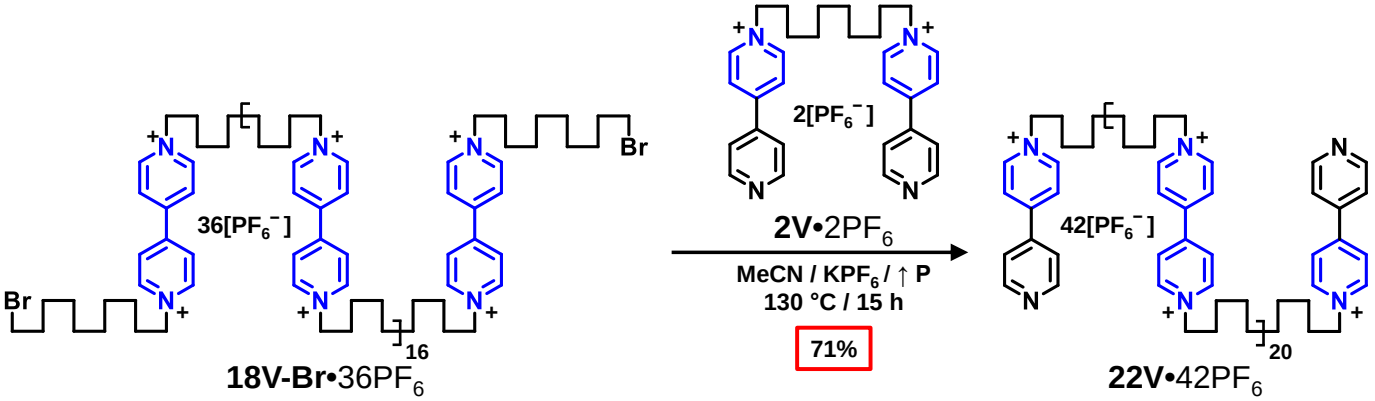
PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **18V•**$34PF_6$ as 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, $(CD_3)_2SO$): δ_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, $(CD_3)_2SO$): δ_C 150.08, 148.62, 145.71, 126.56, 60.95, 30.85, 28.91, 28.52, 25.63.

10) 18V-Br•36PF$_6$



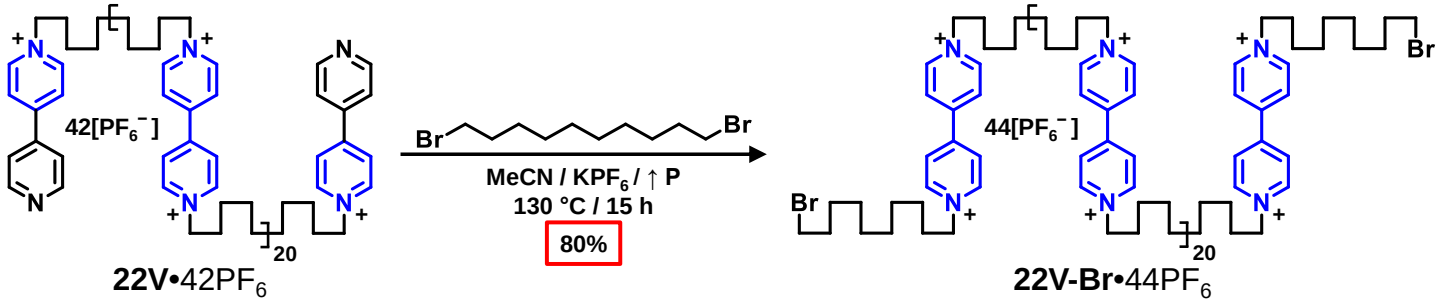
18V•$34PF_6$ (3.00 g, 0.296 mmol, 1 equiv), 1,10-dibromodecane (2.66 g, 8.88 mmol, 30 equiv), and KPF_6 (327 mg, 1.78 mmol, 6 equiv) were dissolved in MeCN (dry, 60 mL, 50 mg·mL^{-1} **18V•**$34PF_6$) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. After completion 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_2O. 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_2O. 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried to yield **18V-Br•**$36PF_6$ as a light brown solid (2.48 g, 77% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_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, $(CD_3)_2SO$): δ_C 148.61, 145.70, 126.56, 60.95, 30.85, 28.91, 28.52, 25.63.

11) 22V•42PF$_6$



18V-Br•36PF$_6$ (1.50 g, 0.138 mmol, 1 equiv), **2V**•2PF$_6$ (2.05 g, 2.764 mmol, 20 equiv) and KPF$_6$ (153 mg, 0.829 mmol, 6 equiv) were dissolved in MeCN (dry, 30 mL, mg·mL^{-1} **18V-Br**•36PF$_6$) 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 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_2O, precipitated as the PF$_6^-$ salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in MeCN (10 mL) and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **22V**•42PF$_6$ as a light brown solid (1.23 g, 71% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V**•2PF$_6$. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ_H 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). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 150.99, 148.63, 145.70, 126.57, 121.89, 60.96, 30.83, 28.87, 28.49, 25.60.

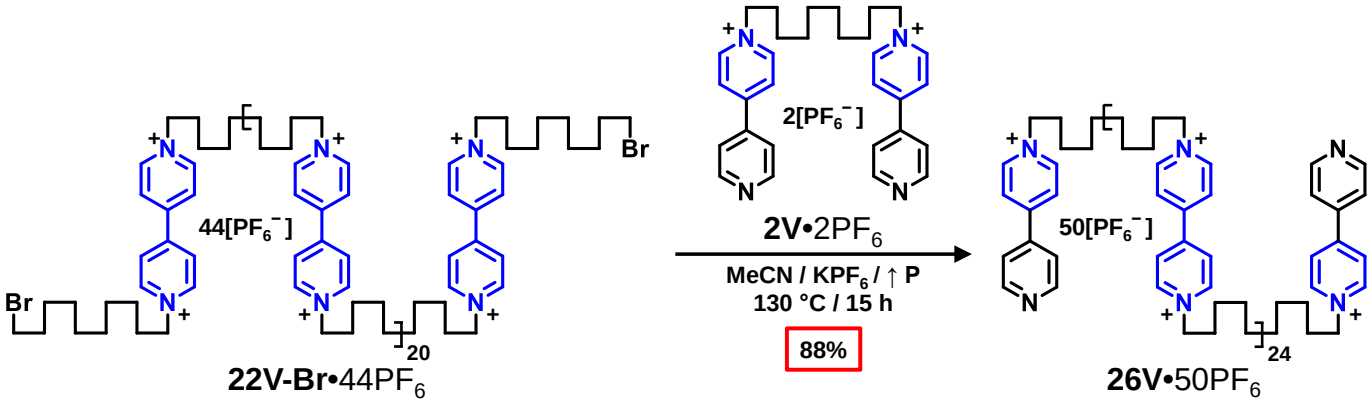
12) 22V-Br•44PF$_6$



22V•42PF$_6$ (1.50 g, 0.120 mmol, 1 equiv), 1,10-dibromodecane (1.08 g, 3.609 mmol, 30 equiv), and KPF$_6$ (133 mg, 0.722 mmol, 6 equiv) were dissolved in MeCN (dry, 30 mL, 50 mg·mL^{-1} **22V**•42PF$_6$) 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_2O. The tubes were centrifuged at 4500 rpm for 2 min. The solution was decanted away,

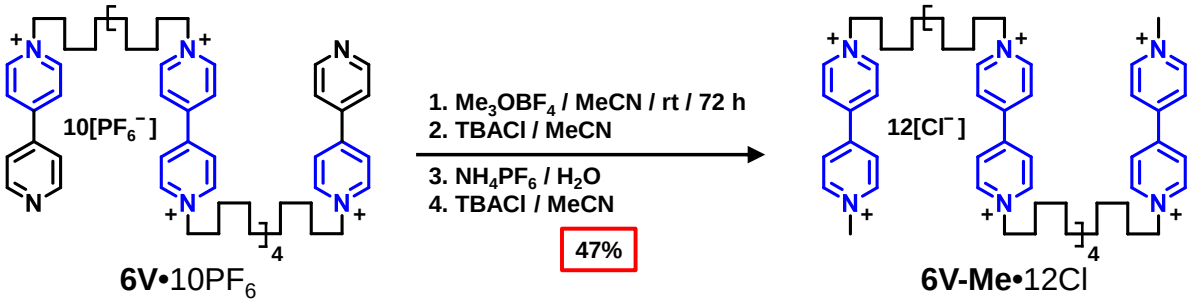
the solid was re-dissolved in a minimal amount of MeCN and diluted to 50 mL with Et_2O. The previous two steps were repeated three times. Two counterion exchanges were performed to ensure complete conversion to the PF_6 salt: the solid was dissolved in MeCN, precipitated as the Cl^- salt using excess TBACl, washed several times with MeCN, and dried. The solid was dissolved in H_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried to yield **22V-Br•**$44PF_6$ as a light brown solid (1.26 g, 80% yield). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): 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). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): 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•50PF$_6$



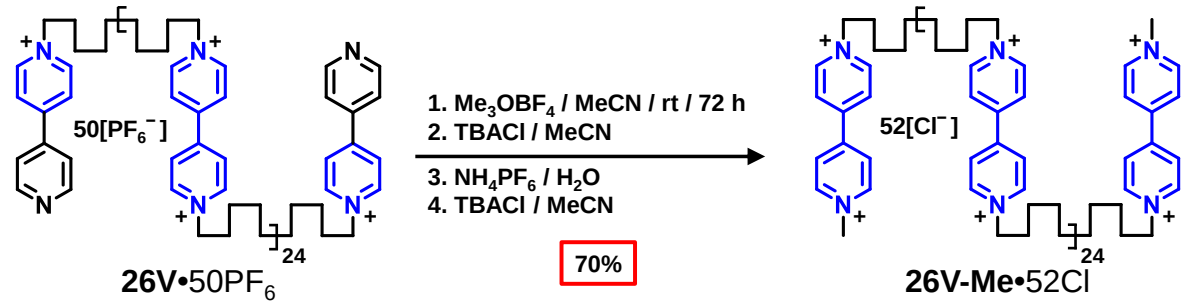
22V-Br•$44PF_6$ (1.26 g, 0.096 mmol, 1 equiv), **2V•**$2PF_6$ (2.13 g, 2.871 mmol, 30 equiv) and KPF_6 (106 mg, 0.574 mmol, 6 equiv) were dissolved in MeCN (dry, 25 mL, 50 mg·mL^{-1} **22V-Br•**$44PF_6$) and heated to 130 °C in a 100 mL glass high-pressure vessel while stirring for 15 h. The reaction vessel was cooled to room temperature and the solution was decanted into four 50 mL centrifuge tubes and diluted to 50 mL with Et_2O. 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 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_2O, precipitated as the PF_6^- salt using excess NH_4PF_6, washed several times with H_2O and dried. The solid was re-dissolved in a minimal amount of Me_2CO and diluted to 50 mL with CH_2Cl_2 and centrifuged at 4500 rpm for 2 min. The solution was decanted away. The previous two steps were repeated five times to yield **26V•**$50PF_6$ as a light brown solid (1.25 g, 88% yield). NMR and TLC analyses were used to confirm complete removal of excess **2V•**$2PF_6$. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): 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). ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ_C 148.62, 145.69, 126.56, 60.96, 30.82, 28.86, 28.48, 25.59.

14) 6V-Me•12Cl



6V•10PF_6 (175 mg, 0.057 mmol, 1 equiv) and Me_3OBF_4 (839 mg, 5.670 mmol, 100 equiv) were dissolved in MeCN (dry, 2.30 mL, 75 mg·mL^{-1} **6V**•10PF_6) and stirred for 3 d at room temperature under N_2. The solution was decanted into two 15 mL centrifuge tubes and diluted to 15 mL with Et_2O. 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 Et_2O. 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 H_2O, NH_4PF_6 was added, and the solid was washed several times with H_2O. The PF_6 salt was redissolved 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). ^{1}H NMR (500 MHz, CD_3OD): δ_H 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). ^{13}C NMR (125 MHz, CD_3OD): δ_C 151.29, 147.07, 128.31, 128.26, 127.91, 63.28, 32.56, 30.35, 30.07, 27.21.

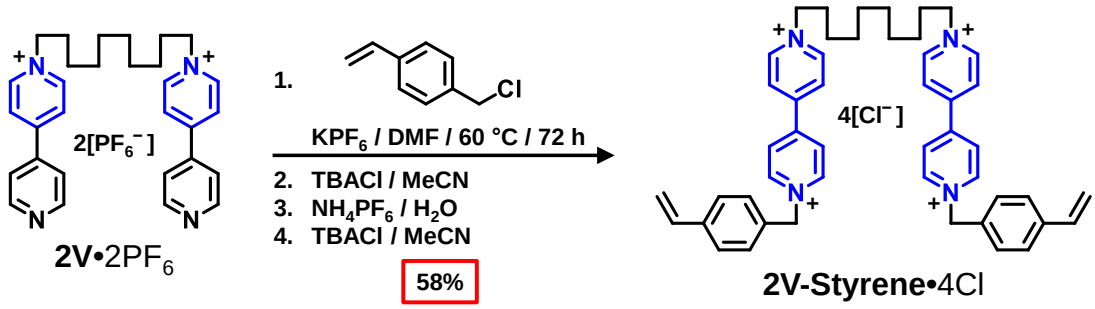
***15)* 26V-Me•52Cl**



26V•50PF_6 (170 mg, 0.012 mmol, 1 equiv) and Me_3OBF_4 (425 mg, 2.875 mmol, 250 equiv) were dissolved in MeCN (dry, 2.25 mL, 75 mg·mL^{-1} **26V**•50PF_6) and stirred for 3 d at room temperature under N_2. The solution was decanted into two 15 mL centrifuge tubes and diluted to 15 mL with Et_2O. 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 Et_2O. 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 H_2O, NH_4PF_6 was added, and the solid was washed several times with H_2O. The PF_6 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_3OD): δ_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_3OD): δ_C 151.28, 147.08, 128.31, 128.26, 127.91, 63.27, 32.57, 30.36, 30.08, 27.22.

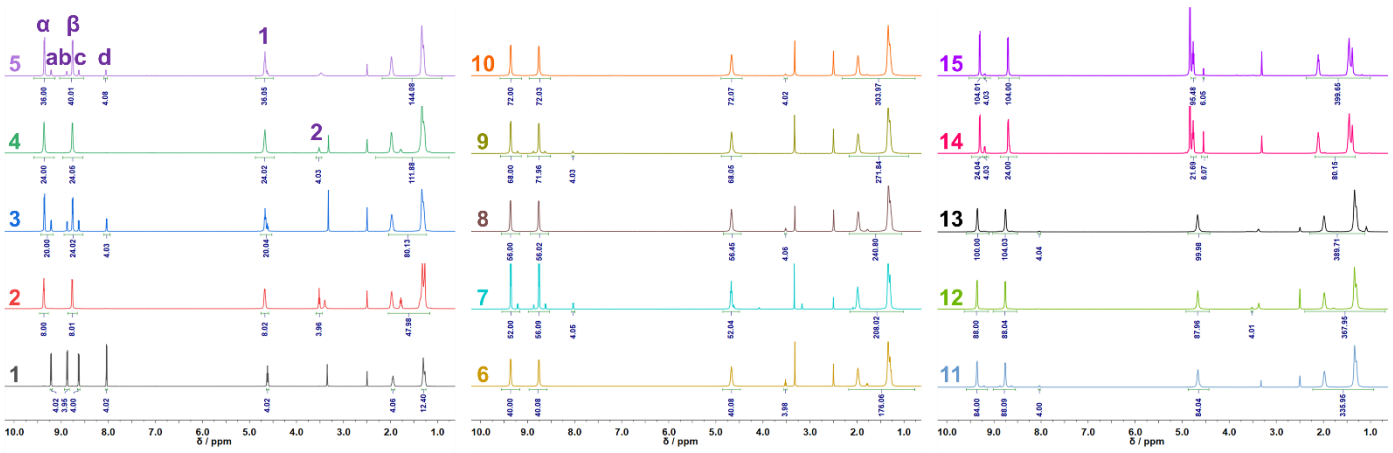
16) 2V-Styrene•4Cl



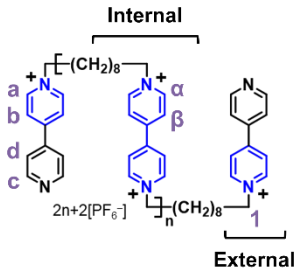
2V•2PF_6 (1.00 g, 1.347 mmol, 1 equiv), 4-vinylbenzyl chloride (6.17 g, 5.69 mL, 40.41 mmol, 30 equiv), and KPF_6 (1.49 g, 8.082 mmol, 6 equiv) were dissolved in DMF (dry, 13 mL, 75 mg·mL^{-1} **2V•**2PF_6) and heated to 60 °C in a 50 mL screwtop round bottom flask at ambient pressure for 3 days. The 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_2O. 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_2O. 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_2O and NH_4PF_6 was added, and the solid was washed several times with H_2O. 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, $(CD_3)_2SO$): δ_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_3OD): δ_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.

Section C. Spectroscopic Characterization

1) Nuclear Magnetic Resonance Spectroscopy



Compound	α+a	β+b+c	d	1	$(CH_2)_8$	α : a	Internal Viologens	External Viologens	DP_n
6V•10PF$_6$	20.00	24.02	4.03	20.04	80.13	3.96:1	4	2	6
10V•18PF$_6$	36.00	40.01	4.08	36.05	144.08	7.82:1	8	2	10
14V•26PF$_6$	52.00	56.09	4.05	52.04	208.02	11.84:1	12	2	14
18V•34PF$_6$	68.00	71.96	4.03	68.05	271.84	15.87:1	16	2	18
22V•42PF$_6$	84.00	88.09	4.00	84.04	335.95	20.00:1	20	2	22
26V•50PF$_6$	100.00	104.03	4.04	99.98	389.71*	23.75:1	24	2	26



Compound	α	β	1	2	$(CH_2)_8$	α : 2	DP_n
2V-Br•4PF$_6$	8.00	8.01	8.02	3.96	47.98	2.02:1	2
6V-Br•12PF$_6$	24.00	24.05	24.02	4.03	111.88	5.96:1	6
10V-Br•20PF$_6$	40.00	40.08	40.08	3.98	176.06	10.05:1	10
14V-Br•28PF$_6$	56.00	56.02	56.45	4.06	240.80	13.80:1	14
18V-Br•36PF$_6$	72.00	72.03	72.07	4.02	303.97	17.91:1	18
22V-Br•44PF$_6$	88.00	88.04	87.96	4.01	367.95	21.95:1	22

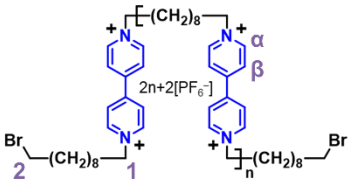


Figure S1: Full ^{1}H NMR (500 MHz) spectra for each iterative product in the synthesis of **26V•**50PF$_6$. **a)** In $(CD_3)_2SO$: (1) **2V•**2PF$_6$, (2) **2V-Br•**4PF$_6$, (3) **6V•**10PF$_6$, (4) **6V-Br•**12PF$_6$, (5) **10V•**18PF$_6$, (6) **10V-Br•**20PF$_6$, (7) **14V•**26PF$_6$, (8) **14V-Br•**28PF$_6$, (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_3OD (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_2SO_4 in H_2O. 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.

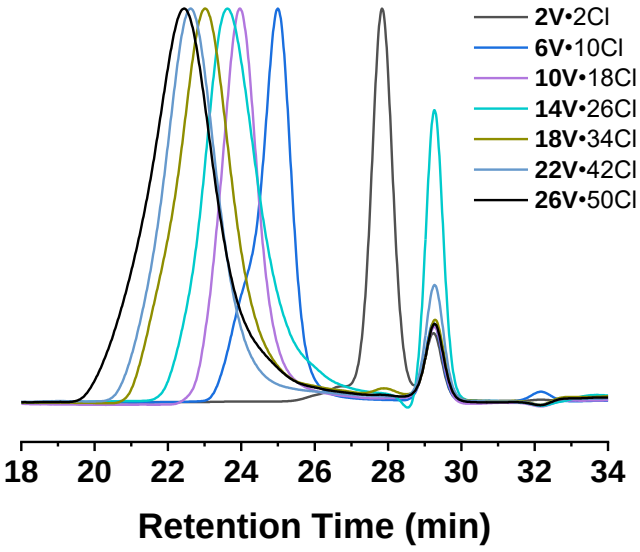


Figure S2: Full GPC traces (dRI) for each iterative bipyridine-capped product in the synthesis of **26V**•50PF_6. From right to left: Na_2SO_4 salt (29.27 min), **2V**•2X (27.83 min), **6V**•10X (24.99 min), **10V**•18X (23.96 min), **14V**•26X (23.62 min), **18V**•34X (23.01 min), **22V**•42X (22.62 min), and **26V**•50X (22.44 min), where where X is Cl, HSO_4, or a mixture of anions.

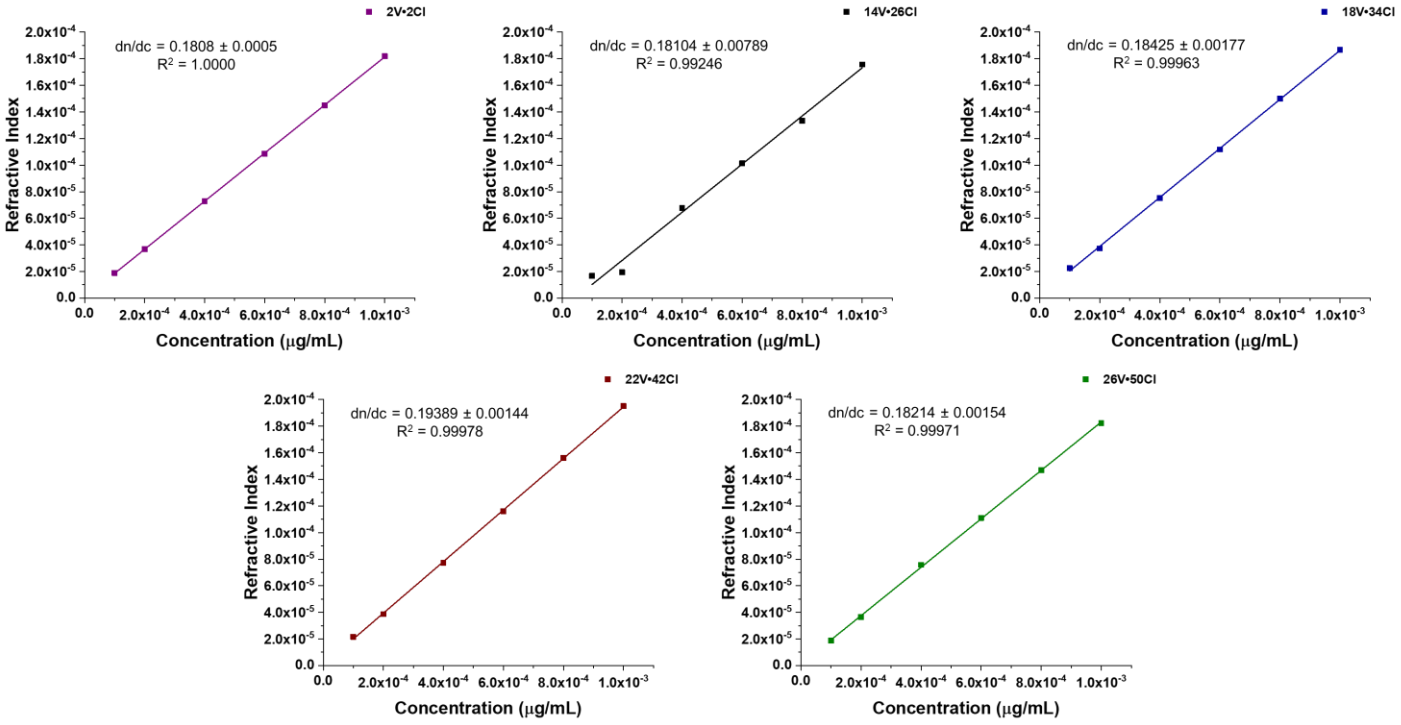


Figure S3: Plots of concentration vs. refractive index for the calculation of dn/dc values for select oligo and polyviolgens. From left to right and top to bottom: **2V**•2Cl, **14V**•26Cl, **18V**•34X, **22V**•42X, and **26V**•50X, where X is Cl, HSO_4, or a mixture of anions.

The refractive index increment, dn/dc, values were determined as follows: a stock solution of each oligo- and polyviologen were prepared in the GPC solvent (0.025 M Na_2SO_4) 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

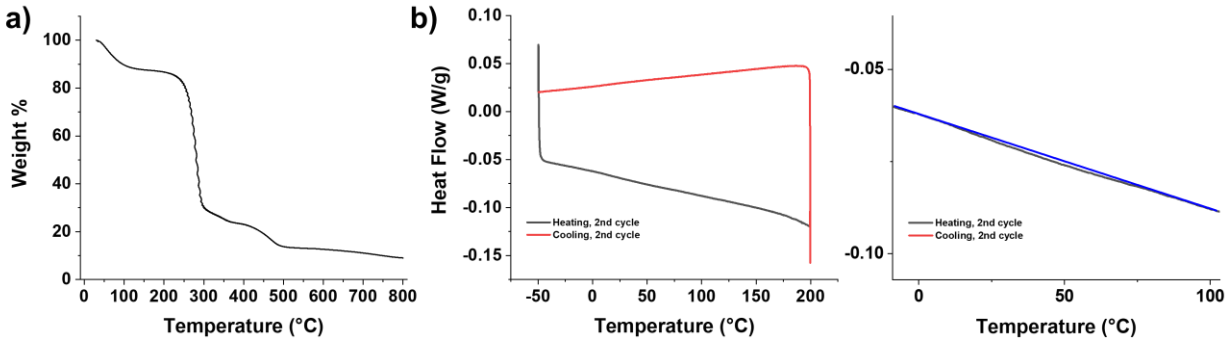


Figure S4: Thermogravimetric analysis (a) and Differential scanning calorimetry (b: zoomed out (left) and zoomed in (right)) of **26V-Me•**52Cl.

4) Powder X-Ray Diffraction (PXRD)

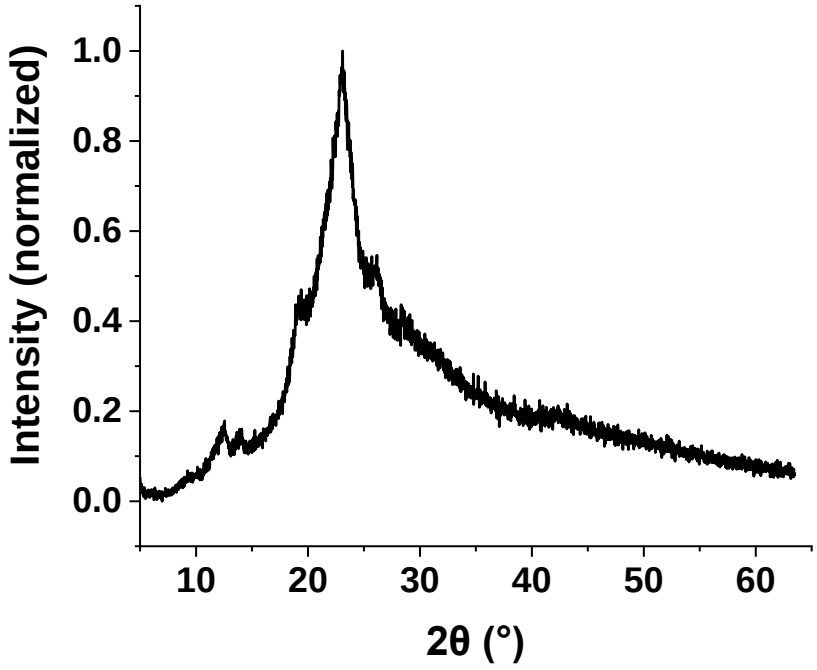


Figure S5: Powder X-ray diffraction of **26V-Me•**52Cl

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 H_2O, neutralized with the addition of 3 µL of 2M HCl, and slightly acidified by the addition of 3 uL 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*-$BuNH_2$), 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 ^{1}H NMR (**Figure S6**) and GPC. The sample degraded using ethanolamine was also analyzed via LC/MS.

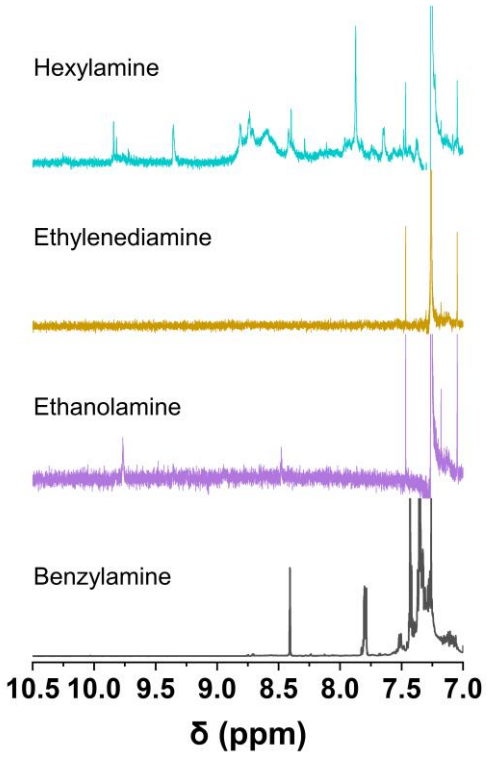


Figure S6: ^{1}H NMR spectroscopic characterization (in $CDCl_3$) of the extraction of 7 d samples with CH_2Cl_2 before the addition of excess NH_4PF_6.

3) Fabrication of Viologen-based Hydrogel Networks

2V-Styrene•4Cl	**0.5 mol %**	**Bisacrylamide**	**0.5 mol %**
Acrylamide (mg)	8450.0	Acrylamide (mg)	8850.0
Crosslinker (mg)	496.0	Crosslinker (mg)	96.0
Ammonium Persulfate (mg)	54.0	Ammonium Persulfate (mg)	54.0
Total mass (mg)	9000.0	Total mass (mg)	9000.0
DMSO (mL)	18.00	DMSO (mL)	18.00

PEG Diacrylate 575	**0.5 mol %**
Acrylamide (mg)	8596.0
Crosslinker (mg)	350.0
Ammonium Persulfate (mg)	54.00
Total mass (mg)	9000
DMSO (mL)	18.00

Tables S1-3: Reagents used for the synthesis of gels containing 0.5 mol % **2V-Styrene•**4Cl, *N,N'*-Bisacrylamide, PEG_{575}-Diacrylate.

A modified procedure[1] 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_2O for 48 h with periodic changes in H_2O to allow for full swelling and removal of unreacted material.

4) Degradation of Viologen-based Hydrogel Networks

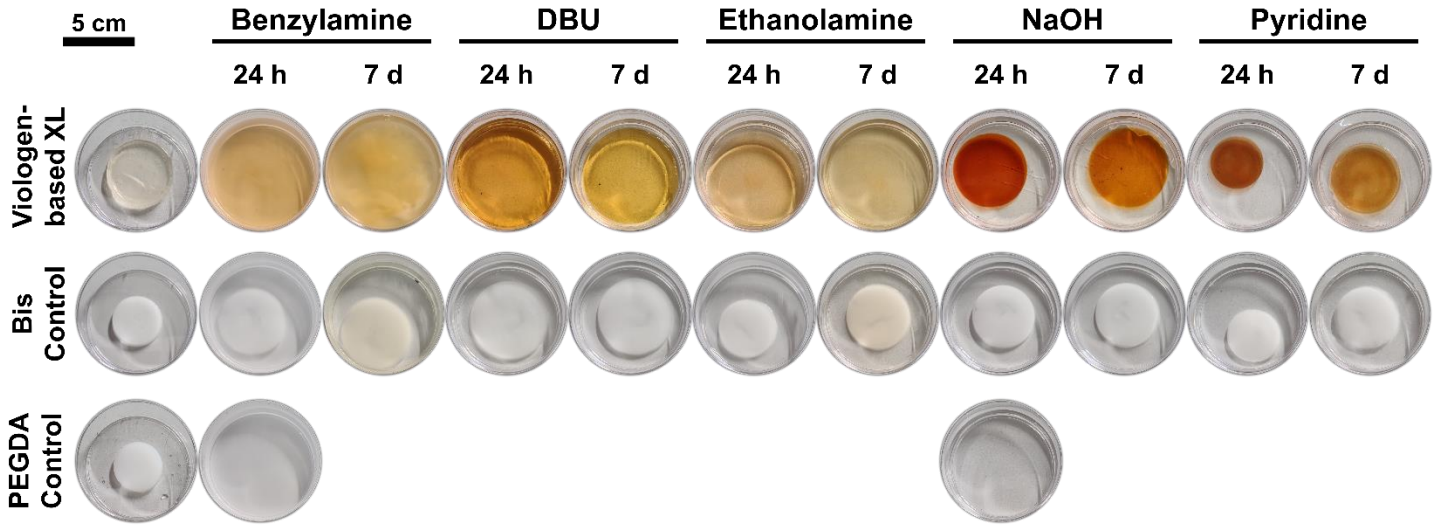


Figure S7: Degradation of hydrogels crosslinked with **2V-Styrene•**4Cl, N,N'-Bisacrylamide, and PEG_{575}-Diacrylate using benzylamine, DBU, ethanolamine, NaOH, and Pyridine after 24 h and 7 d.

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 H_2O 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

Crosslinker	*G′*[a] (Pa)	*G″*[b] (Pa)	*G*[c] (Pa)	ΔG[d]
Viologen EA (24 h)	6.791	2.045	7.092	↓ 172 x
Viologen Control	1223	14.94	1223.09	
Bis EA (24 h)	369.5	54.45	373.5	↑ 1.9 x
Bis Control	199.6	32.58	202.2	

[a] Storage modulus (*G′*), determined at 10% strain. [b] Loss modulus (*G″*), determined at 10% strain. [c] Calculated from *G′* and *G″*. [d] Fold change between the hydrogel soaked in ethanolamine and the hydrogel soaked in MilliQ water.

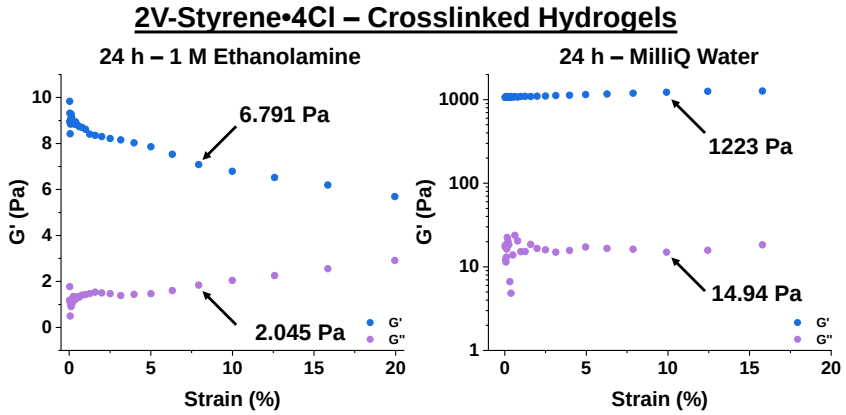


Figure S8: Oscillatory shear rheology at 10 rad·sec^{-1} of a hydrogel crosslinked with **2V-Styrene•**2Cl soaked for 24 h in ethanolamine (left) and MilliQ water (right).

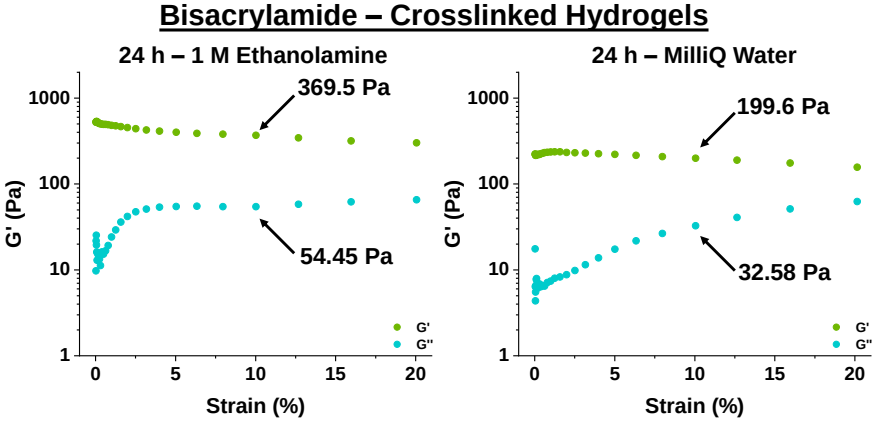


Figure S9: Oscillatory shear rheology at 10 rad·sec^{-1} of a hydrogel crosslinked with **2V-Styrene•**2Cl soaked for 24 h in ethanolamine (left) and MilliQ water (right).

Section E. Additional Figures

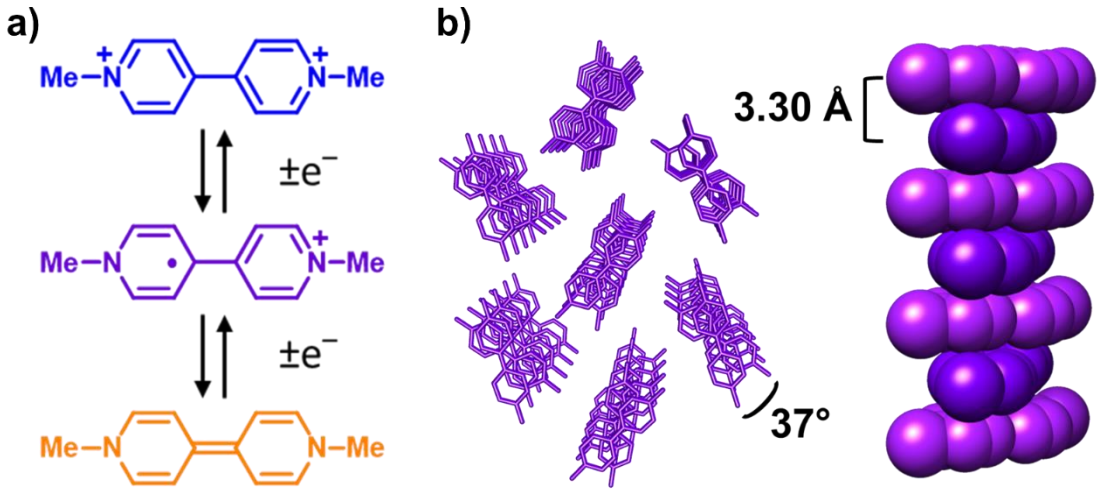


Figure S10: Reduction of viologens and subsequent radical-radical interaction in the solid state[2]

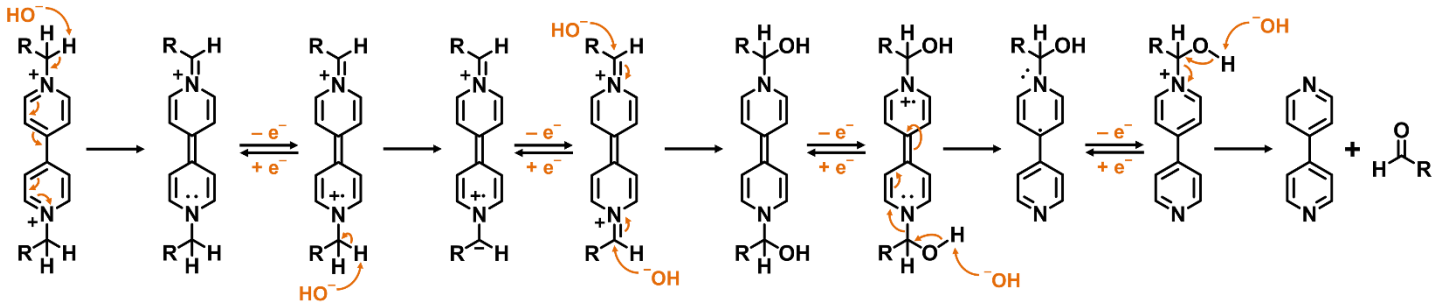


Figure S11: Proposed mechanism of the degradation of viologens by Corwin, Arellano, and Chivvis[3]

Section F. References

1 A. O. Delawder, A. Natraj, N. D. Colley, T. Saak, A. F. Greene and J. C. Barnes, *Supramol. Chem.*, 2019, **31**, 523–531.

2 T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, 1990, **55**, 4127–4135.

3 A. H. Corwin, R. R. Arellano and A. B. Chivvis, *Biochim. Biophys. Acta Bioenerg.*, 1968, **162**, 533–538.