

Supporting Information

A Switchable Single-Molecule Electrochromic Device Derived From A Viologen-Tethered Triazolium-Based Poly(ionic liquid)

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4. Experimental

4.1 Materials. Acetonitrile (CH₃CN, 99.8%, Sigma-Aldrich), 1-Bromo-3-chloropropane (C₃H₆BrCl 99%, Alfa Aesar), 4,4'-Bipyridene, 1-Iodomethane, 1-Iodobutane, 1-iodohexane, 1-Iododecane, Diethyl ether, Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and triazole based PILs were synthesized as described previously²⁵.

4.2 Synthesis of viologen. To a solution of 4,4'-bipyridene was added slowly haloalkane (iodobutane and iodohexane). The solution was allowed to react at 25°C~60°C for 23~72 hrs. Product was precipitated, filtered off, and washed with diethyl ether. After purified by recrystallization with ethanol (for iodobutane) and acetone (for iodohexane), it was isolated as solid colored material. Sample was completely dried under vacuum. Further, the dried sample was reacted with C₃H₆BrCl in acetonitrile for 48 hr at room temperature. The final product was filtered and washed with diethyl ether and finally dried under vacuum. *1-butyl-1'-(3-chloropropyl)-[4,4'-bipyridine]-1,1'-dium iodide* ([C₄C₃bpy]I) ¹H NMR (400 MHz, Methanol-d₄) δ (ppm): 9.13 (d, *J*=7 Hz, 4H), 8.82-8.80 (m, *J*=6.3 Hz, 4H), 4.77-4.67 (m, 4H), 2.11-2.00 (m, 2H), 1.52-1.41 (m, 6H), 1.04-1.00 (td, *J*=7.4 Hz, 3H); *1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-dium iodide* ([C₆C₃bpy]I) ¹H NMR (400 MHz, Methanol-d₄) δ (ppm): 9.17-9.12 (d, 4H), 8.84-8.78 (m, 4H), 4.80-4.66 (m, 4H), 2.14-2.01 (m, 2H), 1.50-1.29 (m, 10H), 0.95-0.88 (t, 3H).

4.3 Synthesis of smart PIL. Synthesized viologen was reacted with various PILs in acetonitrile at 60°C for 60 hr. The product was precipitated with diethyl ether and washed copiously. Dissolved in

acetonitrile and filtered using syringe filter 0.45um PTFE. It was completely dried under vacuum for 24 hrs. Further, they were dissolved in DI water and a certain amount of LiTFSI was added, allowed to react for 24 hrs at 40°C. Solid product deposited on the walls of the flask. Liquid was decanted and washed with diethyl ether. Dissolved with methanol and precipitated with diethyl ether, 2 times. Dissolved with acetonitrile and filtered with 0.45um syringe filter. Solvent removed and completely dried in vacuum. *Poly(3-(1-butyl-1'-(3-propyl)-[4,4'-bipyridine]-1,1'-dium iodide)-4-(2,5,8,11-tetraoxatridecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide)* (TEG-[C₄C₃bpy]TFSI): ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.20-9.19 (d,4H), 8.75-8.74 (d, 4H), 8.61-8.59 (d, 1H), 4.67-4.61 (m, 6H), 4.46-4.44 (m, 4H), 3.77-3.74 (m, 2H), 3.50-3.43 (m, 20H), 1.94-1.87 (m, 2H), 1.34-1.26 (m, 8H), 0.92-0.88 (m, 3H); *Poly(3-(1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-dium iodide)-4-(2,5,8,11-tetraoxatridecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide)* (TEG-[C₆C₃bpy]TFSI): ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.21-9.19 (d,4H), 8.75-8.73 (d, 4H), 8.61-8.59 (d, 1H), 4.67-4.57 (m, 6H), 4.44-4.46 (m, 4H), 3.77-3.76 (m, 2H), 3.49-3.43 (m, 20H), 1.94-1.90 (m, 2H), 1.27 (s, 8H), 0.85-0.82 (m, 3H); *Poly(3-(1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-dium iodide)-4-(2,5,8,11,14,17-hexaoxonadecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide)* (HEG-[C₆C₃bpy]TFSI): ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.20-9.18 (d,4H), 8.75-8.73 (d, 4H), 8.61-8.59 (d, 1H), 4.66-4.56 (m, 6H), 4.47 (m, 4H), 3.78-3.75 (m, 2H), 3.49-3.43 (m, 20H), 1.93-1.92 (m, 2H), 1.27 (m, 8H), 0.85-0.82 (m, 3H).

4.4 Spectral and Thermal Analysis. ¹H NMR (400 MHz) spectra were observed using Varian 400-MR spectrometer in Methanol-d₄ and dimethyl sulfoxide (DMSO-d₆). Differential scanning calorimetry (DSC) was conducted under helium using Mettler Toledo at a heating rate of 20°C min⁻¹.

4.5 Electrochemical studies via cyclic voltammetry. Voltammograms of all samples were obtained using SPELEC (DropSens). Test samples were deposited on DropSens screen printed electrodes (SPE) (ITO10: Working-ITO, Counter-Carbon, Reference-Silver) by drop casting 15 µl of 30 wt. % smart PIL in CH₃CN solution. Samples were completely dried in vacuum. Sample SPEs were loaded in Teflon cell and were scanned from -4V to 4V at various scan rates (20 mV s⁻¹ – 120 mV s⁻¹) to determine the

anodic and cathodic peaks for the reduction-oxidation reaction and to study the electrochemical stability of the device at different cycles.

4.6 Optical and color switching kinetics study.

A solution of 10 wt% smart PIL in CH₃CN (20 μl) was drop casted on 2 ITO glass plates (70–100 Ω/sq resistivity: 25 mm × 25 mm × 1.1 mm, Sigma-Aldrich) each forming a thin film. The deposited samples were dried in vacuum for 24 h to remove solvent. Both ITO were put together sandwiching the smart PIL. Trapped air were removed by degassing it in vacuum at room temperature. The device has an active area of 5.0 cm² and an average overall device thickness of 2.23 mm. Transmittance spectra of the samples were obtained using amperometry coupled with a spectrometer (SPELEC).

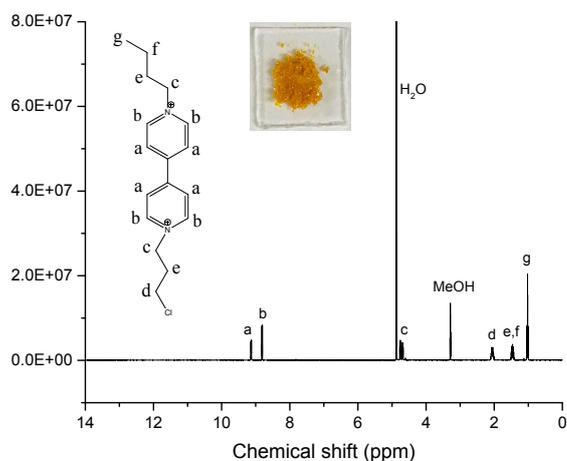


Figure S1. ¹H NMR spectrum and chemical structure of *1-butyl-1'-(3-chloropropyl)-[4,4'-bipyridine]-1,1'-dium iodide* ([C₄C₃bpy]I) with image (inset) of actual compound

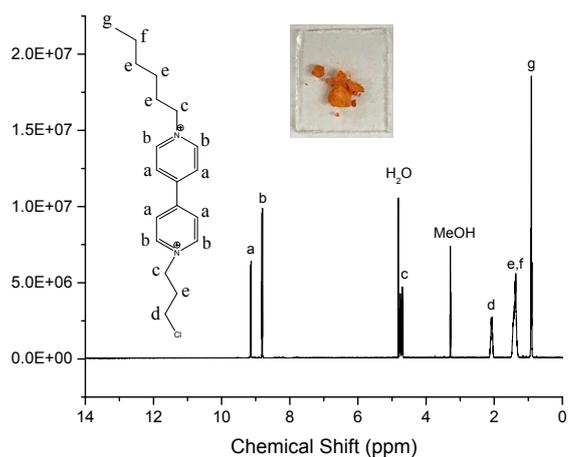


Figure S2. ^1H NMR spectrum and chemical structure of *1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-dium iodide ([C6C3bpy]I)* with image (inset) of actual compound

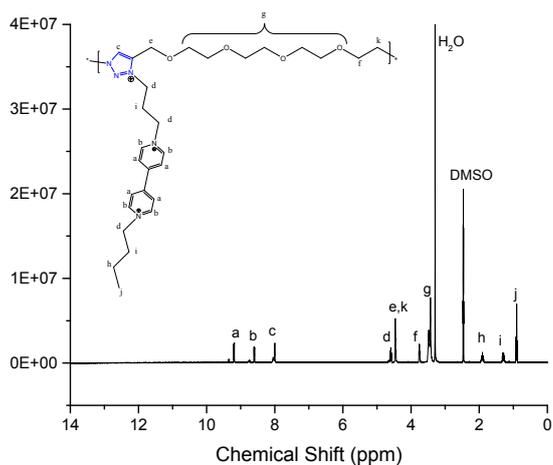


Figure S3. ^1H NMR spectrum and chemical structure of *Poly(3-(1-butyl-1'-(3-propyl)-[4,4'-bipyridine]-1,1'-dium iodide)-4-(2,5,8,11-tetraoxatridecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide) (TEG-[C₄C₃bpy]TFSI)*

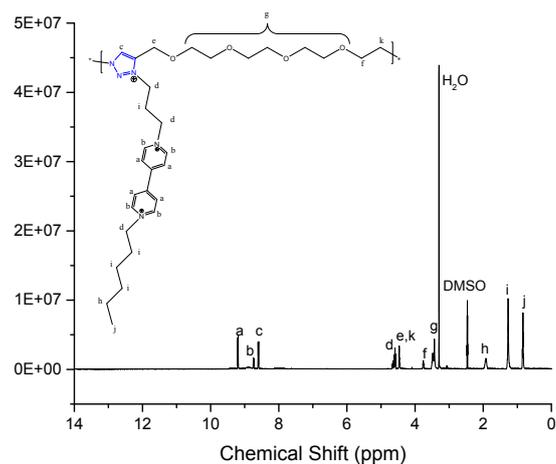


Figure S4. ^1H NMR spectrum and chemical structure of *poly(3-(1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-diium iodide)-4-(2,5,8,11-tetraoxatridecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide)* (TEG-[C₆C₃bpy]TFSI)

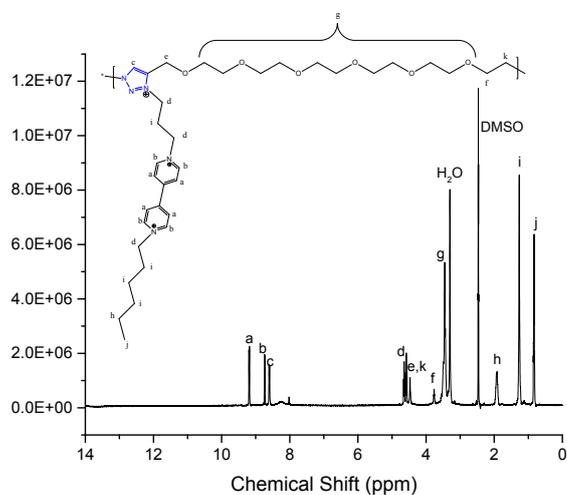


Figure S5. ^1H NMR spectrum and chemical structure of *poly(3-(1-(3-chloropropyl)-1'-hexyl-[4,4'-bipyridine]-1,1'-diium iodide)-4-(2,5,8,11,14,17-hexaoxonadecyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide)* (HEG-[C₆C₃bpy]TFSI)

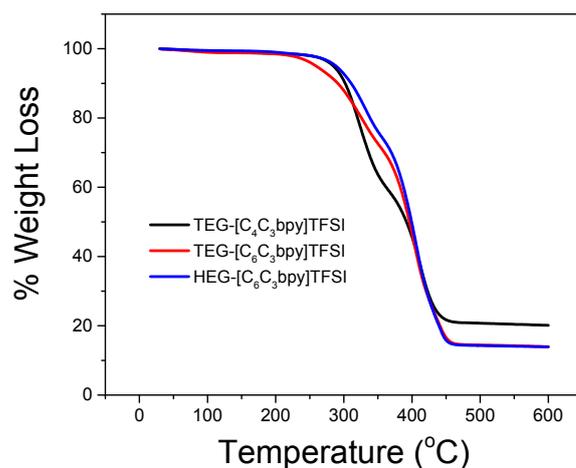


Figure S6. Thermal profile of smart PILs obtained from TGA

Table S1. Physical properties of smart PILs

Smart PIL	Glass Transition	Degradation Temperature at 10% weight Loss, T_{d10} (°C)
	Temperature	
	T_g (°C)	
(TEG-[C ₄ C ₃ bpy]TFSI)	-24.2	301
(TEG-[C ₆ C ₃ bpy]TFSI)	-28.7	290
(HEG-[C ₆ C ₃ bpy]TFSI)	-27.0	310

Table S2. Optical property of smart PILs at initial and 1000th cycle.

Smart PIL	Initial Cycle		1000 th Cycle	
	λ (nm)	ΔT (%)	λ (nm)	ΔT (%)
(TEG-[C ₄ C ₃ bpy]TFSI)	630	10.1	654	6.1
(TEG-[C ₆ C ₃ bpy]TFSI)	605	21.6	602	21.0
(HEG-[C ₆ C ₃ bpy]TFSI)	616	18.1	612	8.2