Supplementary Information

Redox-active Polymer-Grafted Particles as Redox Mediators for Enhanced Charge Transport in Solution-State Electrochemical Systems

Mohd Avais^a, Ratul Mitra Thakur^c, Evan Fox^b, Jodie L. Lutkenhaus^{ac*}, Emily Pentzer^{ab*}

a: Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77840, USA.

b: Department of Chemistry, Texas A&M University, College Station, Texas 77840, USA.

c: Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77840, USA.

*Email: jodie.lutkenhaus@tamu.edu, emilypentzer@tamu.edu

Experimental Section

Materials

2,2,6,6-Tetramethyl-4-piperidyl methacrylate (\geq 98%, 31582-45-3), allyl bromide (~98%, 106-95-6), meta-chloroperoxybenzoic acid (77%, 937-14-4), 4,4'-di-(5-nonyl)-2,2'-bipyridine (97%, 142646-58-0), and copper bromide (98%, 7787-70-4) were obtained from TCI chemicals. γ -Aminopropyl triethoxysilane (APS) (99%, 919-30-2), triethylamine (\geq 99.5%, 121-44-8), sodium sulfate (ACS reagent, \geq 99.0%, anhydrous, powder, 7757-82-6), sodium hydride (90%, 7646-69-7), isopropyl alcohol (\geq 98%, 67-63-0), trimethoxysilane (95%, 2487-90-3), sodium bicarbonate (ACS reagent, \geq 99.7%, 144-55-8), azobisisobutyronitrile (98%, 78-67-1), 4-Hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (95%, 2226-96-2), dichloromethane (~99%, 75-09-2), methanol (99.8%, 67-56-1), hexanes (\geq 98.5%, 110-54-3), THF (ACS reagent, \geq 99.0% 109-99-9), acetonitrile (HPLC Plus, \geq 99.9%, 75-05-8), toluene (anhydrous, 99.8%, 108-88-3) and acetone (67-64-1) were obtained from MilliporeSigma. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) (99.5%, 90076-65-6), silicon wafer, and 2-bromoisobutyryl bromide (97%, 20769-85-1) were obtained from Fischer Scientific. Non-porous silica particles (20 nm, 99.5%) were obtained from SkySpring Nanomaterials, Inc., Deuterated chloroform (\geq 99.8 atom % D, 865-49-6) was received from Cambridge Isotope. All other chemicals were used as received without further purification.

Characterization

Fourier transform infrared (FTIR) spectra were obtained using a JASCO FTIR spectrometer, model FTIR-4600LE MidIR with a universal ATR mode accessory (diamond/ZnSe). The data are reported with a wavenumber range of 500-4000 cm⁻¹ with 32 scans. ¹H NMR spectra were recorded on Bruker 400 MHz NMR spectrometers, using CDCl₃ as a solvent and residual chloroform peak as reference. EPR spectroscopy experiments were completed using a Bruker EMX-EPR spectrometer at room temperature (all samples prepared at 1 mM dispersions in chloroform). Thermogravimetric analysis (TGA) was carried out under N₂ using a TA Instruments TGA 5500 heating from room temperature to 700 °C: ramp 20 °C/min to 120 °C, isothermal 5 min, ramp 20 °C/min to 700 °C. X-ray photoelectron spectroscopy (XPS) was performed using an Omicron X-ray photoelectron spectrometer employing an Mg-sourced Xray beam at 15 kV with aperture 3. Particle size studies were performed using a Horiba Partica LA-960 particle sizer. Molecular weights of polymers were obtained by size exclusion chromatography (TOSOH GPC): tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 0.8 mL/min at 30 °C column temperature and polystyrene standards were used for column calibration. Overlap concentration of the PTMA were determined using a rheometer (TA Instruments HR-2 Rheometer) with plate SST ST 40 mm at 25 °C. A flow sweep from 0.1 to 1000 s⁻¹ was performed in doublet for each sample. From these analyses, the apparent viscosity (n) and viscosity/shear rate profiles were analyzed using TRIOS software (TA Instruments). The surface morphology of the modified silica particles was investigated using a FEI Quanta 600 FE-SEM with an accelerating voltage of 20.0 kV. To study the morphology and size of modified particle silicon wafer was drop casted with extremely diluted solution of particle (concentration >0.1 mg/mL in chloroform) then dried at 80 °C temperature for 12 hours. Prior to investigation, modified particle samples were coated with an 8 nm thin layer of platinum. Transmission electron microscopy (TEM) analyses were performed using a JEOL TEM at an accelerating voltage of 100 kV. The TEM samples were prepared for analyses by drop casting the particles dispersed in chloroform onto carbon grids TEM Window (TED PELLA, INC. 200 meshes Cu) then drying under ambient conditions overnight.

Modification of silica particles with TEMPO containing monomer

The synthesis of 3-(4-oxy-TEMPO)propylsilane was carried out as follows: 4-allyloxy-TEMPO (212 mg, 1 mmol) was synthesized according to literature-reported procedure¹ and subsequently was added to a mixture of 0.5 mg of chloroplatinic acid and 8.0 mg of iso-propanol in a reaction vessel cooled with ice. Over a period of 15 minutes, 244 mg (2 mmol) of trimethoxysilane was added to the mixture. The

reaction mixture was then heated at 60 °C for 6 hours to ensure completion. Following solvent evaporation under reduced pressure, the mixture was taken forward without further purification.

For the grafting of 3-(4-oxy-TEMPO)propylsilane on silica particles, calcined SiO₂ (250 mg) were placed under reduced pressure for 24 hours at 120 °C then subsequently suspended in 10 ml of dry toluene. Then, 3-(4-oxy-TEMPO)propyltrimethoxysilane (87 mg) was added to the suspension, and the mixture was refluxed for 12 hours. The resulting SiO₂-TEMPO was collected by filtration, washed with toluene, and dried under vacuum.

Modification of silica particles with TEMPO containing polymers

<u>Synthesis of APTES-Br Initiator.</u> The APTES-Br initiator was synthesized according to a known procedure:² A solution of 3-aminopropyltriethoxysilane (APTES) (1.8 mL, 8 mmol) in dry toluene (10 mL) was cooled to 0 °C then triethylamine (TEA) (1.2 mL, 8 mmol) was added. Concurrently, a solution of dry toluene (100 mL) containing 2-bromoisobutyryl bromide (1 mL, 8 mmol) was prepared and added dropwise under constant stirring. The reaction mixture was stirred for 3 hours at 0 °C, then an additional 12 hours at room temperature. The mixture was filtered to remove salts, and the filtrate was placed under reduced pressure to remove solvent unreacted TEA. ¹H-NMR (CDCl₃): 6.80 (s, 1H, NH), 3.7 (t, 6H, CH₃CH₂OSi), 3.20 (t, 2H, CH₂NH), 1.88 (q, 6H, CH₃C), 1.59 (m, 2H, CH₂), 1.16 (t, 9H, CH₃CH₂OSi), 0.58 (t, 2H, SiCH₂).

<u>Modification of silica particles with APTES-Br.</u> Initiator-modified SiO₂ particles (i.e., APTES-Br) were synthesized following a modified reported procedure.³ Commercially available SiO₂ particles were dried in a furnace at 500 °C for 4 hours under an inert atmosphere to remove water and any other adsorbed solvents. The SiO₂ particles were then suspended in dry toluene and heated at reflux under a nitrogen atmosphere. A slight excess (1.5 molar equivalents) of APTES-Br initiator was added to the toluene suspension, and the mixture was refluxed for 24 hours to allow for surface functionalization. The initiator-modified SiO₂ particles were isolated via centrifugation and washed with toluene to remove any unreacted or adsorbed initiators. This washing procedure was repeated three times to ensure complete removal of non-grafted initiators. The modified particles were dried under vacuum.

<u>ATRP onto silica particles.</u> ATRP on silica particles was performed using a modified reported procedure.^{3, 4} APTES-Br particles (0.250 g), CuBr (1.25 mg, 8.7×10^{-3} mmol), dNbipy (7.15 mg, 1.75×10^{-2} mmol) and ethyl 2-bromoisobutyrate (0.75 µl, 5.1×10^{-3} mmol) were added to a dried Schlenk flask equipped with a stir bar. TMPM (1.8 g) and p-xylene (5 mL) were then added via syringe, and the solution was degassed by three consecutive cycles of freeze-pump-thaw. Following this, the mixture was

vigorously stirred and sonicated to ensure a homogeneous suspension of particles, after which the flask was heated to 90 °C for 12 hours. Samples were periodically withdrawn using a N₂-flushed syringe, and monomer conversion was monitored by ¹H NMR, utilizing xylene as an internal standard. Subsequently, the resulting SiO₂-PTMPM-5k composite was isolated by filtration and washed with acetone, with the washing step being repeated three times to ensure complete removal of non-grafted polymers. Finally, the purified, modified particles were dried under vacuum. Using the same procedure, two different molecular weight grafted polymers (SiO₂-PTMPM-2.5k and SiO₂-PTMPM-5k) were synthesized using varying amounts of (monomer:initiator) ratios of 15:1 and 60:1, respectively.

<u>Isolation of grafted PTMPM by removal of silica particle core.</u> The isolation of grafted PTMPM from silica particles (SiO₂-PTMPM-2.5k/5k) was conducted as follows: 100 mg of the PTMPM grafted particles were suspended in 2 mL of toluene, followed by the addition of 30 mg of Aliquot 336 as a phase transfer catalyst. Subsequently, 2 mL of a 5% aqueous solution of hydrofluoric acid (HF) was added, and the resulting mixture was stirred for 3 hours. After stirring, the organic layer containing the grafted polymers was isolated then the polymer precipitation into hexanes. The precipitated polymer was isolated by filtration then solvent removed under reduced pressure. The isolated polymers were characterized SEC for determination of molecular weight distribution.

<u>Oxidation of grafted PTMPM polymers.</u> The oxidation of grafted PTMPM from silica particles (SiO₂-PTMPM-2.5k/5k) was conducted following a modified procedure.⁴ SiO₂-PTMPM-2.5k/5k (250 mg) modified silica particles were dispersed in a 5 mL dichloromethane solution of meta-chloroperoxybenzoic acid (mCPBA, 0.326 g, 1.9 mmol) for 15 min to obtain a SiO₂-PTMA-2.5/5k. Following reaction completion, the SiO₂-PTMA-2.5k/5k modified particles were isolated via centrifugation and washed three times by suspension-reprecipitation. The purified modified particles were dried under vacuum.

Synthesis of bulk PTMA



Scheme S1. Synthesis of PTMA via free radical polymerization, followed by oxidation

The poly(2,2,6,6-tetramethylpiperidine methacrylate) (PTMPM) was synthesized following a modified reported procedure.⁵ Commercially available azobisisobutyronitrile (AIBN) was initially recrystallized in methanol, filtered, and dried under reduced pressure. The recrystallized AIBN (0.109 g, 0.67 mmol) was then added to a 10 mL toluene solution of 2,2,6,6-tetramethylpiperidine methacrylate (5.0 g, 22 mmol). The resulting mixture was heated at 75 °C for 48 hours under a nitrogen atmosphere. Upon completion of the reaction, the mixture was precipitated in hexanes then washed three times. The final polymer was dried under reduced pressure at room temperature. The polymers were collected and the secondary amine oxidized to nitroxide radical with 2 molar equiv. of mCPBA for 3 hours. The combined polymer-oxidizer solution was washed with an aqueous sodium carbonate solution, and the organic fraction was collected. The polymer was then precipitated in hexanes, filtered, and dried under reduced pressure overnight. Notably, the color of the polymer changed from white to orange after oxidation.

Calculation for determining brush conformation

 $h \sim (N * \sigma^{\frac{1}{2}})^{x}$(S1)

h: brush height

N: degree of polymerization (D_P)

σ: grafting density

If $0.6 \le x \le 1$: semi-dilute brush conformation

If x = 1: concentrated brush region

The above empirical relation was reported.⁶ Both the SiO₂-PTMA-5k and SiO₂-PTMA-2.5k are in semidilute brush conformation.

Table S1: Grafting density, brush height, degree of polymerization, calculated x for SiO₂-PTMA-5k and SiO₂-PTMA-5k particles.

Sample	Grafting density (chain/nm ²)	Brush height (h) (nm)	N	x (from equation S1)
SiO ₂ -PTMA-5k	0.38	~7.5	20	0.8
SiO ₂ -PTMA-2.5k	0.68	~4.5	10	0.7

Calculation for determining radius of gyration

 $R_a \approx N^{0.5}$(S2)

R_g: Radius of gyration

N: Degree of polymerization

The above empirical relation was reported to calculate the radius of gyration of grafted polymer.⁷ The calculated R_g were 3.16 nm and 4.47 nm for SiO₂-PTMA-2.5k and SiO₂-PTMA-5k, respectively.

C*: Overlap concentration

N_A: Avogadro's number

Rg: Radius of gyration

The above relation was reported to determine the radius of gyration of polymer.⁸ The determined R_g for PTMA was 14.4 nm.

Electrochemical characterization

All electrochemical characterization was conducted in a three-electrode configurations. The glassy carbon electrode was the working electrode; silver wire was the quasi-reference electrode; and platinum wire was the counter electrode. The electrode area for the glassy carbon electrode was 0.196 cm^2 . 10 ml of 0.1 M lithium bis(trifluoromethane) sulfonimide (LiTFSI) in acetonitrile (ACN) was used as an electrolyte for all the experiments. PTMA, SiO₂-TEMPO, SiO2-PTMA-2.5k, and SiO₂-PTMA-5k particles were added to the PTMA solution at different concentrations to perform solution state measurements. Cyclic voltammetry (CV) was performed from a scan rate of 2 mV/s to 100 mV/s (each 2 cycles) from a potential window of 0.2 V to 1 V *vs*. QRE. Electrochemical impedance spectroscopy (EIS) was performed at the half-wave potential (~ 0.67 to 0.73 V *vs*. QRE) from a frequency range of 100 kHz to 10 mHz, applying a voltage perturbation of 10 mV. Chronoamperometry was performed between a potential range of 0.2 V to 1 V *vs* QRE, where the working electrode is kept at 0.2 V initially and a step potential (to 1 V) is applied for 60 sec, followed by another step potential to 0.2 V. SiO₂-grafted nanoparticles (NPs) were added on the basis of repeat units grafted on the SiO₂ nanoparticles.



Figure S1. FTIR spectra of allyl bromide (top) and 4-allyloxy TEMPO (bottom).



Figure S2. FTIR spectra of bromo isobutrate (top) and APTES-Br initiator (bottom).



Figure S3. ¹H NMR spectra of APTES-Br initiator in CDCl₃.



Figure S4. a) IR spectra of calcined silica particles (top) and APTES-Br initiator modified particles (bottom). b) TGA spectra of calcined silica particles (top) and APTES-Br initiator modified particles (bottom).



Figure S5. ¹H NMR spectrum for monomer conversion for SiO₂-PTMPM-2.5k using dimethoxyethane as an internal standard.



Figure S6. ¹H NMR spectrum for monomer conversion for SiO₂-PTMPM-5k using dimethoxyethane as an internal standard.



Figure S7. GPC chromatograms of isolated PTMPM from silica particles for (a) PTMPM-2.5k, and (b) PTMPM-5k.



Figure S8. TGA spectra of SiO₂.



Figure S9. EPR spectrum of calcined silica particles.



Figure S10. a) GPC chromatogram of bulk PTMA, b) IR spectra of TEMPO methacrylate (top) and PTMA (bottom).



Figure S11. Determination of the overlap concentration of PTMA in the 0.1 M lithium bis(trifluoromethane) sulfonimide (LiTFSI) in acetonitrile via rheometry.



Figure S12. Viscosity of 6 mM bulk PTMA in 0.1 M LiTFSI in acetonitrile with different amounts of SiO₂-PTMA-5k grafted particles added (2.5%, 5%, 10%, and 15% of the total repeat unit of the system).



Figure S13. a) Cyclic voltammetry of PTMA at different concentration, b) oxidation peak current and half wave potential ($E_{1/2}$) of PTMA at different concentration in 0.1 M LiTFSI in acetonitrile at a scan rate of 10 mV/s.



Figure S14. Cyclic voltammograms PTMA and PTMA with successive addition of SiO₂-PTMA-5k particles. The scan rate was 10 mV/s. SiO₂-PTMA-5k were added to PTMA solutions at concentrations of a) 6 mM, b) 7.2 mM in 0.1 M LiTFSI in acetonitrile. SiO₂-PTMA-5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S15. Cyclic voltammograms PTMA and PTMA with successive addition of SiO₂-PTMA-2.5k particles. The scan rate was 10 mV/s. SiO₂-PTMA-2.5k were added to PTMA solutions at concentrations of a) 6 mM, b) 7.2 mM in 0.1 M LiTFSI in acetonitrile. SiO₂-PTMA-2.5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S16. Cyclic voltammograms PTMA and PTMA with successive addition of SiO_2 -TEMPO particles. The scan rate was 10 mV/s. SiO_2 -TEMPO were added to PTMA solutions at concentrations of a) 6 mM and b) 7.2 mM in 0.1 M LiTFSI in acetonitrile. SiO_2 -TEMPO were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S17. a) Chronoamperometry for PTMA at different concentration using an applied potential step from 0.2 to 1 V versus QRE, b) Cottrell plots for oxidation and reduction at different PTMA concentration dispersed in 0.1 M LiTFSI in acetonitrile.



Figure S18. Cottrell plots from chronoamperometry of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO₂-PTMA-5k particles using an applied potential step from 0.2 to 1 V versus QRE in 0.1 M LiTFSI in acetonitrile. SiO₂-PTMA-5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S19. Cottrell plots from chronoamperometry of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO₂-PTMA-2.5k particles using an applied potential step from 0.2 to 1 V versus QRE in 0.1 M LiTFSI in acetonitrile. SiO₂-PTMA-2.5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S20. Cottrell plots from chronoamperometry of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO₂-TEMPO particles using an applied potential step from 0.2 to 1 V versus QRE in 0.1 M LiTFSI in acetonitrile. SiO₂-TEMPO were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%,10% and 15% of total repeat unit of the system.



Figure S21. Apparent diffusion coefficient (D_{app}) and heterogenous rate constants (k°), see Table S1 and Table S2. a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO₂-PTMA-5k particles. c) 6 mM PTMA and d) 7.2 mM PTMA with successive addition of SiO₂-PTMA-2.5k particles.

The parameters were calculated using Cottrell equation and Nicholson methods as reported in previous study.⁹



Figure S22. Nyquist plot of different PTMA concentrations from EIS at the half-wave potential, applying a 10 mV alternating voltage from 100 kHz to 10 mHz in 0.1 M LiTFSI in acetonitrile.



Figure S23. Nyquist plots of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO_2 -PTMA-5k particles from EIS at the half-wave potential, applying a 10 mV alternating voltage from 100 kHz to 10 mHz in 0.1 M LiTFSI in acetonitrile. SiO_2-PTMA-5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%, 10% and 15% of total repeat unit of the system.



Figure S24. Nyquist plots of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO_2 -PTMA-2.5k particles from EIS at the half-wave potential, applying a 10 mV alternating voltage from 100 kHz to 10 mHz in 0.1 M LiTFSI in acetonitrile. SiO_2-PTMA-2.5k were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%, 10% and 15% of total repeat unit of the system.



Figure S25. Nyquist plots of a) 6 mM PTMA and b) 7.2 mM PTMA with successive addition of SiO_2 -PTMA-TEMPO particles from EIS at the half-wave potential, applying a 10 mV alternating voltage from 100 kHz to 10 mHz in 0.1 M LiTFSI in acetonitrile. SiO_2 -PTMA-TEMPO were added to the PTMA solution in successive way such that repeat units derived from grafted particles constitute of 5%, 10% and 15% of total repeat unit of the system.

Modified silica	% of Repeat unit		6 mM PTMA		7.2 mM PTMA		
particle coming from modified silica particles	$I_{p \text{ Oxidation}} \\ (\mu A/cm^2)$	$\begin{array}{c} I_{p \ Reduction} \\ (\mu A / cm^2) \end{array}$	Ip Oxidation/Ip Reduction	$\begin{array}{c} I_{p \; Oxidation} \\ (\mu A/cm^2) \end{array}$	$I_{p \text{ Reduction}} (\mu A/cm^2)$	$I_{p \text{ Oxidation}}/I_{p}$ Reduction (
a :e	0%	113.97	108.50	1.05	135.14	124.75	1.08
SiO ₂ - TEMPO	5 %	103.78	101.51	1.02	140.73	134.62	1.05
	10%	117.31	107.62	1.09	141.35	135.88	1.04
	15%	120.35	114.89	1.05	163.99	158.38	1.04
SiO ₂ - PTMA- 2.5k	0%	113.97	108.50	1.05	135.14	124.75	1.08
	5 %	122.85	117.48	1.05	144.15	134.21	1.07
	10%	124.43	119.11	1.05	154.82	144.85	1.07
	15%	129.61	123.62	1.05	155.81	147.47	1.06
SiO ₂ - PTMA- 5k	0%	113.97	108.50	1.05	135.14	124.75	1.08
	5 %	131.18	124.23	1.06	145.09	132.55	1.09
	10%	130.63	125.21	1.05	154.07	144.67	1.06
	15%	134.72	130.03	1.04	162.31	151.08	1.07

Table S2. Anodic peak current ($I_{p \text{ Oxidation}}$), cathodic peak current ($I_{p \text{ Reduction}}$), and peak current ration for PTMA and PTMA with successive addition of modified silica particles.

Table S3. Anodic peak current ($I_{p \text{ Oxidation}}$), cathodic peak current ($I_{p \text{ Reduction}}$), and peak current ratio for PTMA and SiO2-PTMA-5k at different scan rates.

	$6 \text{ mM PTMA} + \text{SiO}_2\text{-PTMA-5k} (5\%)$				
Scan rate (mV/s)					
	$I_{p \text{ Oxidation}}(\mu \text{A/cm}^2)$	$I_{p \text{ Reduction}} (\mu A / cm^2)$	I _{p Oxidation} /I _{p Reduction}		
5	91.43	82.73	1.10		
10	131.18	124.23	1.06		
25	194.71	185.06	1.05		
50	273.52	260.89	1.05		
100	345.38	344.01	1.00		

PTMA				
Concentration				
	D_{app} (cm ² /s)	k _{ex,app}	kº (cm/s)	
		(L/mol.s)		
3 mM	$1.063 \times 10^{-06} \pm$	$3.324 \times 10^{11} \pm$	$4.809 \times 10^{-04} \pm$	
	0.002×10 ⁻⁰⁶	0.008×10^{11}	0.006×10 ⁻⁰⁴	
6 mM	9.033×10 ⁻⁰⁷ ±	$1.411 \times 10^{11} \pm$	$4.432 \times 10^{-04} \pm$	
	0.039×10 ⁻⁰⁷	0.004×10^{11}	0.008×10^{-04}	
7.2 mM	$8.568 \times 10^{-07} \pm$	$1.116 \times 10^{11} \pm$	$5.013 \times 10^{-04} \pm$	
	0.021×10 ⁻⁰⁷	0.002×10^{11}	0.006×10^{-04}	
9 mM	$8.207 \times 10^{-07} \pm$	$8.549 \times 10^{10} \pm$	$4.224 \times 10^{-04} \pm$	
	0.048×10^{-07}	0.051×10^{10}	0.012×10^{-04}	

Table S4. Apparent diffusion coefficient (D_{app}) and heterogenous rate constant (k^{o}) for PTMA at different concentrations in 0.1 M LiTFSI in ACN

	% of Repeat						
Modified	unit coming	6 mM PTMA			7.2 mM PTMA		
silica	from						
particle	modified						
	silica	D_{app} (cm ² /s)	k _{ex.app}	kº (cm/s)	D_{app} (cm ² /s)	k _{ex.app}	kº (cm/s)
	particles	-rr 、	(L/mol.s)		-rr ()	(L/mol.s)	~ ~ ~
	0%	$9.033 \times 10^{-07} \pm$	$1.411 \times 10^{11} \pm$	$4.432 \times 10^{-04} \pm$	$8.568 \times 10^{-07} \pm$	$1.116 \times 10^{11} \pm$	$5.013 \times 10^{-04} \pm$
		0.039×10 ⁻⁰⁷	0.004×10^{11}	0.008×10^{-04}	0.021 ×10 ⁻⁰⁷	0.002×10 ¹¹	0.006 ×10 ⁻⁰⁴
	5 %	$7.881 \times 10^{-07} \pm$	$1.171 \times 10^{11} \pm$	$3.471 \times 10^{-04} \pm$	$8.862 \times 10^{-07} \pm$	$1.098 \times 10^{11} \pm$	$3.337 \times 10^{-04} \pm$
SiO ₂ -		0.049×10 ⁻⁰⁷	0.007×10^{11}	0.011×10^{-04}	0.051×10 ⁻⁰⁷	0.006×10 ¹¹	0.009 ×10 ⁻⁰⁴
TEMPO	10%	$7.70 \times 10^{-07} \pm$	$1.084{ imes}10^{11}{ \pm}$	$3.130 \times 10^{-04} \pm$	$8.737 \times 10^{-07} \pm$	$1.024 \times 10^{11} \pm$	$3.313 \times 10^{-04} \pm$
		0.063×10 ⁻⁰⁷	0.009×10 ¹¹	0.603×10 ⁻⁰⁴	0.026×10 ⁻⁰⁷	0.003×10 ¹¹	0.005×10 ⁻⁰⁴
	15%	$7.687 \times 10^{-07} \pm$	$1.022{ imes}10^{11}{ \pm}$	$1.439 \times 10^{-04} \pm$	$9.971 \times 10^{-07} \pm$	$1.104 \times 10^{11} \pm$	$1.953 \times 10^{-04} \pm$
		0.051×10 ⁻⁰⁷	0.007×10^{11}	0.005×10^{-04}	0.011×10^{-07}	0.001×10^{11}	0.001×10^{-04}
	0%	$9.033 \times 10^{-07} \pm$	$1.411 \times 10^{11} \pm$	$4.43{\times}10^{\text{-}04}{}\pm$	$8.568 \times 10^{-07} \pm$	$1.116 \times 10^{11} \pm$	$5.013 \times 10^{-04} \pm$
		0.039×10 ⁻⁰⁷	0.004×10^{11}	0.008×10^{-04}	0.021 ×10 ⁻⁰⁷	0.002×10^{11}	0.006×10 ⁻⁰⁴
	5 %	$9.410 \times 10^{-07} \pm$	$1.397{ imes}10^{11}{ \pm}$	$5.253 \times 10^{-04} \pm$	$1.021 \times 10^{-06} \pm$	$1.264 \times 10^{11} \pm$	$5.471 \times 10^{-04} \pm$
SiO ₂ -		0.011×10 ⁻⁰⁷	0.001×10^{11}	0.003×10 ⁻⁰⁴	0.002×10 ⁻⁰⁶	0.002×10^{11}	0.006×10 ⁻⁰⁴
PTMA-	10%	$8.795 \times 10^{-07} \pm$	$1.238{ imes}10^{11}{ \pm}$	$4.373{ imes}10^{-04}{ imes}1$	$9.771 \times 10^{-07} \pm$	$1.145 \times 10^{11} \pm$	$4.609 \times 10^{-04} \pm$
2.5k		0.066×10 ⁻⁰⁷	0.009×10^{11}	0.016×10 ⁻⁰⁴	0.029×10 ⁻⁰⁷	0.003×10 ¹¹	0.007×10^{-04}
	15%	$8.019 \times 10^{-07} \pm$	$1.066{ imes}10^{11}{ \pm}$	$4.849 \times 10^{-04} \pm$	$9.303 \times 10^{-07} \pm$	$1.030 \times 10^{11} \pm$	$4.498 \times 10^{-04} \pm$
		0.016×10 ⁻⁰⁷	0.002×10^{11}	0.049×10 ⁻⁰⁴	0.074×10^{-07}	0.008×10^{11}	0.017×10 ⁻⁰⁴
SiO ₂ - PTMA- 5k	0%	$9.033 \times 10^{-07} \pm$	$1.411 \times 10^{11} \pm$	$4.432 \times 10^{-04} \pm$	$8.568 \times 10^{-07} \pm$	$1.116 \times 10^{11} \pm$	$5.013 \times 10^{-04} \pm$
		0.039×10 ⁻⁰⁷	0.004×10^{11}	0.008×10^{-04}	0.021×10 ⁻⁰⁷	0.002×10^{11}	0.006×10 ⁻⁰⁴
	5 %	$1.041 \times 10^{-06} \pm$	$1.546 \times 10^{11} \pm$	$5.526 \times 10^{-04} \pm$	$8.571 \times 10^{-07} \pm$	$1.061 \times 10^{11} \pm$	$4.317 \times 10^{-04} \pm$
		0.009×10 ⁻⁰⁶	0.012×10 ¹¹	0.023×10 ⁻⁰⁴	0.005×10 ⁻⁰⁷	0.005×10 ¹¹	0.001×10 ⁻⁰⁴
	10%	$9.813 \times 10^{-07} \pm$	$1.381 \times 10^{11} \pm$	$5.364 \times 10^{-04} \pm$	$8.956 \times 10^{-07} \pm$	$1.050 \times 10^{11} \pm$	$4.413 \times 10^{-07} \pm$
		0.013×10 ⁻⁰⁷	0.002×10^{11}	0.004×10 ⁻⁰⁴	0.029×10 ⁻⁰⁷	0.004×10^{11}	0.007×10 ⁻⁰⁷
	15%	$8.985 \times 10^{-07} \pm$	$1.195 \times 10^{11} \pm$	$3.707 \times 10^{-04} \pm$	$8.735 \times 10^{-07} \pm$	$9.669 \times 10^{10} \pm$	$4.358 \times 10^{-04} \pm$
		0.025×10 ⁻⁰⁷	0.003×10 ¹¹	0.005×10^{-04}	0.034×10 ⁻⁰⁷	0.038×10^{10}	0.009×10 ⁻⁰⁴

Table S5. Apparent diffusion coefficient (D_{app}) and heterogenous rate constant (k^{o}) for PTMA and PTMA with successive addition of modified silica particles



Figure S26. Comparison of electrochemical behaviors for two PTMA systems: 6.35 mM PTMA solution and a modified 6 mM PTMA system with the addition of 0.35 mM SiO₂-PTMA-5k particles. (a) Cyclic voltammetry results, (b) electrochemical impedance spectroscopy, and (c) Cottrell plot analysis.

References

(1) Brunel, D.; Fajula, F.; Nagy, J.; Deroide, B.; Verhoef, M.; Veum, L.; Peters, J.; Van Bekkum, H. Comparison of two MCM-41 grafted TEMPO catalysts in selective alcohol oxidation. *Applied Catalysis A: General* **2001**, *213* (1), 73-82.

(2) Sun, Y.; Ding, X.; Zheng, Z.; Cheng, X.; Hu, X.; Peng, Y. Surface initiated ATRP in the synthesis of iron oxide/polystyrene core/shell nanoparticles. *European Polymer Journal* **2007**, *43* (3), 762-772.

(3) von Werne, T.; Patten, T. E. Atom Transfer Radical Polymerization from Nanoparticles: A Tool for the Preparation of Well-Defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/"Living" Radical Polymerizations from Surfaces. *Journal of the American Chemical Society* **2001**, *123* (31), 7497-7505. DOI: 10.1021/ja010235q.

(4) Lin, H.-C.; Li, C.-C.; Lee, J.-T. Nitroxide polymer brushes grafted onto silica nanoparticles as cathodes for organic radical batteries. *Journal of Power Sources* **2011**, *196* (19), 8098-8103.

(5) Nakahara, K.; Iwasa, S.; Satoh, M.; Morioka, Y.; Iriyama, J.; Suguro, M.; Hasegawa, E. Rechargeable batteries with organic radical cathodes. *Chemical Physics Letters* **2002**, *359* (5-6), 351-354.

(6) Conrad, J. C.; Robertson, M. L. Shaping the structure and response of surface-grafted polymer brushes via the molecular weight distribution. *JACS Au* **2023**, *3* (2), 333-343.

(7) Lettow, J. H.; Yang, H.; Nealey, P. F.; Rowan, S. J. Effect of graft molecular weight and density on the mechanical properties of polystyrene-grafted cellulose nanocrystal films. *Macromolecules* **2021**, *54* (22), 10594-10604.

(8) Poling-Skutvik, R.; Mongcopa, K. I. S.; Faraone, A.; Narayanan, S.; Conrad, J. C.; Krishnamoorti, R. Structure and dynamics of interacting nanoparticles in semidilute polymer solutions. *Macromolecules* **2016**, *49* (17), 6568-6577.

(9) Ma, T.; Easley, A. D.; Thakur, R. M.; Mohanty, K. T.; Wang, C.; Lutkenhaus, J. L. Nonconjugated Redox-Active Polymers: Electron Transfer Mechanisms, Energy Storage, and Chemical Versatility. *Annual Review of Chemical and Biomolecular Engineering* **2023**, *14*, 187-216.