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Voltage Activated Adhesion through Donor-Acceptor Dendrimers

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For Table of Contents use only (3.5 in W × 1.375 in H)

ABSTRACT: Previous investigations on voltage-activated adhesives were restricted to aqueous solvents, where current directed crosslinking competed with water electrolysis. Replacing aqueous would expand applications of electrocuring technology and avoid excessive foaming, but many organic solvents have high ohmic resistances that prevent electrical conduction. These impediments were overcome through internal grafting of ferrocene (Fc) and diazirine (Dz) donor-acceptor pairs on fifth generation polyamidoamine (G5-PAMAM) dendrimers, forming G5-Fc-Dz cografed conjugates, where Fc internal additives provided an instantaneous conductive hole (+) network towards the redox conversion of diazirine to carbene insertion adhesion in non-toxic organic solvents of DMSO, DMF, and PEG400. Size exclusion chromatography and ^1H , ^{19}F NMR evaluated the formulations before and after electrocuring to quantitate grafting ratios and crosslinked dendrimers. Cyclic voltammetry confirmed the retained redox behavior of grafted Fc and Dz. Real-time electro-rheology established the dependence of crosslinking kinetics and adhesion strength on applied voltage. Liquid G5-Fc₁₅-Dz₃₀ conjugates reached gelation within 2 min and with a storage modulus up to 3.4 ± 0.5 kPa. For the first time, a model system demonstrates the design components necessary towards organic, voltage-activated one-pot adhesives. This has broad implications for adhesives, cosmetics, implantable biomaterials, and flexible biosensors.

▪ INTRODUCTION

The adhesives global market is estimated to be worth 108B USD by 2020 and is currently dominated by two-part adhesives, consisting of liquid organic resin (*e.g.* epoxy, acrylate or urethane monomers) and a hardener responsible for initiation and propagation of the resin polymerization¹. Development of one-pot adhesives aims to replace two-part adhesives, as one-pot formulations have the advantages of on-demand curing, extended pot-life,

automation, and simplified hardware for application. One-pot adhesives are activated (initiation of resin polymerization) through an external stimulus such as temperature or irradiation, *e.g.* snap-cure thermosets^{2,3}, electron beam/gamma-cured epoxy⁴, or photocured acrylates^{5,6}. Despite the advances in electropolymerization and electroconducting polymers⁷⁻⁹, no structural adhesives (*e.g.* epoxy or acrylate resins) have been reported that allow one-pot electrocuring or adhesives that could be initiated by voltage with current controlled material properties. Perhaps the most pressing challenge preventing such formulations is the electrically insulating properties of the liquid monomer and crosslinked matrix resins — reminiscent of organic solvents. Electrically conductive adhesives, utilized in bonding of microelectronics¹⁰⁻¹², require conductive particle additives, including silver flakes, metal whiskers, and carbon nanotubes. Recently, our group has developed one-pot adhesive based on carbene crosslinking mechanisms, with activation by UV photocuring¹³ and low voltage (2-10V) electrocuring^{14, 15}. N-heterocyclic carbenes allow the mediated polymerization of cyclic esters, epoxides, and acrylates, potentially allowing voltage-activated carbenes to induce the initiation of these thermoset adhesives¹⁶⁻¹⁸. The electrocuring adhesive is composed of two essential moieties: (1) water/organic-soluble dendrimer, poly(amidoamine) (PAMAM),¹⁹ which allows a high probability of intermolecular crosslinking while minimizing high viscosity linear entanglements; (2) diazirine (Dz) functional group, which generates carbene²⁰⁻²³ for crosslinking either upon 320-370 nm UV irradiation^{13, 24, 25} or under -1.6 V¹⁴. Viscoelastic properties were tunable upon Dz grafting density, dendrimer/solvent w/w ratios, or applied joules (light dose), when followed by photorheometry. The maximum reported storage modulus (G') reached ~ 100 kPa within 4 min of UV exposure.¹³ Voltage was also serendipitously observed to cure this adhesive, which is defined as electrocuring.¹⁴ Electro curing has the advantage of bonding opaque substrates where the adhesive material properties are conceivably microelectronically controlled. The PAMAM-g-diazirine

dendrimer currently serves as a model system towards the development of electrocuring structural adhesives that can crosslink on-demand.

However, in terms of electrocuring PAMAM-g-diazirine formulations, the following limitations are noted: 1) limited to aqueous solutions with high salt concentrations of 0.2 to 2 M for sufficient solvent conductivity; 2) maximum storage modulus of 1 kPa vs. 100 kPa for photocuring formulations; 3) minimum electrocuring of -1.6 V in aqueous solutions simultaneously activates water electrolysis (-1.3 V) where oxygen and hydrogen evolution contributes to foaming and weakens bulk mechanical properties; 4) oxidation species generated from water electrolysis is hypothesized to activate carbene. All limitations would be curtailed or reduced if the aqueous solvent/electrolyte is replaced with a non-aqueous alternative.

To reformulate the electrocuring adhesive for organic solvents, the following three hypotheses are generated: 1) to mediate the high resistance of organic solvents, internal (polymer grafting) of donor-acceptor additives are required for electron transduction and contactless electrochemistry, the donor-acceptor theory from metal organic frameworks (MOFs)²⁶ inspires this design; 2) by removing water electrolysis and its associated foaming, a higher probability of intermolecular crosslinking yields increased storage modulus; 3) organic miscible peroxides will replace electrolysis oxidants hypothesized for diaziridine oxidation and subsequent carbene formation. Herein, we demonstrate electrocuring of an adhesive in organic solvent for the first time. The concept of electrocuring in aqueous solution and organic solvent is compared in **Figure 1a**.

Figure 1. (a) Scheme of electrocuring in aqueous vs. organic solvents. Aqueous solutions liberate hydrogen and oxygen gases, causing excessive foaming. (b) Synthetic route of intermediate conjugates, G5-Fc_X (X = 15%), and cografted conjugates, G5-Fc_X-Dz_Y (X = 15%, Y = 7%, 15%, 30%).

EXPERIMENTAL SECTION

Materials. G5-PAMAM dendrimer (5th generation, 30 kDa, 128 primary amines) was supplied by Dendritech, USA. 3-[4-(bromomethyl)phenyl]-3-(trifluoromethyl)-diazirine (aryl diazirine) was supplied by TCI, Tokyo. Chlorocarbonyl ferrocene was supplied by

PICHEMICALS, China. Conjugates were synthesized by following reported procedures.^{13, 27}
Disposable TE100 3-electrode chip procured from Zensor® R&D Company, Taipei, China.

Synthesis of Cografted G5-Fc₁₅-Dz_Y Conjugates. Synthesis has been previously published.²⁷ Briefly, chlorocarbonyl ferrocene was grafted to G5-PAMAM at a fixed grafting ratio (15%) to primary amines (denoted as G5-Fc₁₅) in anhydrous methanol, followed by aryl diazirine with grafting ratio ranging from 7%, 15% and 30% (labelled as G5-Fc₁₅-Dz_Y, Y = 7%, 15% and 30%) with respect to surface amines. G5-Fc₁₅ and G5-Fc₁₅-Dz_Y final products were obtained by precipitating in CHCl₃/Hexane (1/4 in v/v).

SEC-MALS-UV Analysis. An Agilent 1100 HPLC is equipped with the in line detectors: UV/Vis, multi-angle light scattering (MALS, Wyatt Technology Corporation, US), and refractive index (RI, Agilent Technologies, Santa Clara, CA, USA) detectors. PLGel aqueous MIX-H column in a 60°C oven was applied for size exclusion chromatography with 1% w/v formic acid eluent (flow rate 1 mL/min). Dendrimer samples were dissolved in DMSO and then diluted eluent²⁸ to 2 mg/mL followed by 0.2 µm syringe filtration before injection (50 µL). Dn/dc of 0.185²⁹ was applied for PAMAM and conjugates¹⁴. The UV extinction coefficients are reported in **Table S3**, ABS spectra are reported in **Figure S11**.

NMR Spectroscopy Analysis. All desired conjugates/cografted conjugates were analyzed with NMR (Bruker Advance) at 400 MHz with DMSO-d₆ utilized as solvent. MestReNova software was applied for the peak assignment and peak integration of ¹H NMR, ¹³C NMR, ¹⁹F NMR and 2D NMR spectra.

Cyclic Voltammetry (CV). PocketSTAT potentiostat with Ivium Technologiesm software was employed to record the cyclic voltammograms. The custom built electrochemical cell was placed in a Faraday cage, equipped with a platinum counter electrode and a Ag/AgCl reference electrode (filled with saturate LiCl ethanol solution). Glassy carbon (GC, 3-mm diameter, prepared with 1.5, 0.3 and 0.05µm Al₂O₃ polishing)

served as working electrode (WE). The cyclic voltammograms data were recorded in DMSO solution with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte, at the scan rate of 100 mV/s. All cyclic voltammograms were scanned from negative potential to positive potential. The concentrations applied for aryl diazirine was 15 mM, 2.5 wt% in DMSO electrolyte solution for dendrimer samples. CV scanning was performed over three cycles and the second cycle was collected.

Electrorheology Instruments for Electrocurving Viscoelasticity Measurements.

Dynamic rheometry (Physica MCR 501 Rheometer, USA) coupled with a portable potentiostat (PocketSTAT potentiostat, Ivium Technologiesm, USA) was applied to activate electrocuring of dendrimer samples (**Figure 2a**). A polypropylene-based Zensor® chip, embedded with a 3-mm diameter GC as working electrode (WE), an outer annular crescent GC as counter electrode (CE), and a Ag/AgCl pellet as reference electrode (RE), was selected as electrode platform. A stainless steel rheometer probe with 5-mm diameter parallel-plate geometry “PP05” (Anton Paar, USA) was selected as measuring probe as it covers the 3-mm diameter WE. Dissolved sample (50 wt% conjugates in DMSO solution, or 25 wt% in DMF and PEG400 solution with 0.1 M Bu_4NPF_6 electrolyte) was pipetted onto Zensor® chip. The PP05 probe (0.15 mm, 0.30 mm, and 0.60 mm gap sizes) determined the sample geometry. The loss modulus and the storage modulus of the formulations were recorded at 1 Hz strain rate for the amplitude sweep and 10% amplitude under oscillatory dynamic analysis (**SI-Video1**). The potentiostat was applied to maintain the activation voltage at -3 V or -5 V. Measurement period was controlled within 60 min to avoid the Zensor® chip’s insulator coating being dissolved/damaged or the embedded WE being swollen.

Electrorheology Tack Adhesion Measurements. After voltage applied, PP05 probe tensile force measurement was recorded at a velocity of 50 $\mu\text{m/s}$. The maximum load before

failure is reported as the tack adhesion (N/cm^2), normalized by the working electrode area (3 mm diameter).

COMSOL Simulation of Electric Potential Distribution. Electric potential distribution between the work and counter electrode Zensor® electrode were generated using FEM simulation software (COMSOL V5.1). The 3D CAD model was designed in Autodesk Fusion 360 and imported as an assembly into COMSOL. The electrodes were assigned properties of glassy carbon (conductivity $2\text{E}+5 \text{ S m}^{-1}$ and relative permittivity 10)³⁰ and Zensor® substrate assigned nonconductive property (conductivity 0 S m^{-1}). A cylinder mimicking the conductivity of DMSO (conductivity $2\text{E}-7 \text{ S m}^{-1}$, relative permittivity 46.7)³¹ was in contact with the electrode surface. -5 V was assigned to working electrodes. The electric voltage generated between the two electrodes was generated in 3D. During post-processing, the 3D data was visualized in 2D at YZ plane and a contour map was generated for the electric field. Following assumption were made in the simulation: 1) the potential applied in the working electrode is uniform, and 2) the base on the insulator is grounded.

▪ RESULTS

Selection of DMSO, Grafted Ferrocene, and Dendrimer Allows a Conductive Medium. DMSO is selected as the organic solvent as it satisfied the following prioritized parameters: 1) an aprotic solvent that dissolves G5-PAMAM at high concentrations; 2) large electrochemical window of 5V; ³²⁻³⁴ and 3) acts as a hydroxyl radical scavenger, preventing interference by electrolysis of trace water^{35, 36}. Other alkanols are miscible with G5-PAMAM, but are not aprotic while dimethylformamide (DMF) has limited solubility.³⁷ DMSO allows a high concentration of 50% w/w ratio of G5-PAMAM dendrimers and all grafted derivatives, which have a similar molality as the aqueous solutions prepared previously.¹⁴ Ferrocene (Fc) is selected as the internal additive due to its redox-stable

property and its role in electron transduction, known to promote electron transfer^{38, 39} when cooperating with self-assemble monolayers⁴⁰, polymers⁴¹⁻⁴⁴, polymer brushes^{39, 45, 46}, dendrimers⁴⁷⁻⁵² and proteins^{53, 54}. Dendrimers are the preferred polymer backbone, as they limit linear polymer entanglement with the intended design of low viscosity at high concentration of 10-50 wt%. G5-PAMAM dendrimers have primary amines group constrained to the surface, which facilitates grafting and intermolecular covalent crosslinking. The cogenerated G5-Fc₁₅-Dz_Y conjugates are prepared by a simple two-step synthesis as seen in **Figure 1b**.²⁷ Fc is grafted to the G5-PAMAM at a fixed grafting ratio of 15% to the G5-PAMAM amines (G5-Fc₁₅) and diazirine (Dz) is subsequently grafted on G5-Fc₁₅. Grafting the Dz on first or Fc grafting above 15% leads to solubility issues in methanol (reaction solvent) or DMSO (electrocuring solvent). The conjugation percentages of the attached dual functionalities were estimated by NMR and SEC-MALS-UV independently. G5-PAMAM and intermediate conjugates are characterized by ¹H NMR and listed in **Figure S1a**. Reaction efficiency and final grafting ratios are determined by ¹H NMR and displayed in **Figure S1b**. Size exclusion chromatography (SEC) with the appropriate detectors allows molar mass determination of grafted conjugates, and independent mass determinations of PAMAM, Fc grafting, and Dz grafting, as seen **Figure S2a-S2c**. The theoretical and calculated values via ¹H NMR and SEC are compared in **Table S1**. ¹⁹F NMR analysis of G5-Fc₁₅-Dz₃₀ probes for diazirine activation, taking advantage of the -CF₃ R-group, is shown in **Figure S4**. A customized electrorheology setup (**Figure 2a**) is applied to activate the crosslinking and record the *in-situ* real-time kinetics for both loss and storage modulus, followed by tack adhesion. Cyclic voltammetry (CV) evaluates the redox behavior of Fc and Dz after dendrimer immobilization, to determine any shifts in voltage.

G5-Fc₁₅-Dz₃₀ Display Faster Crosslinking Kinetics and Increased Storage Modulus than G5-Dz₃₀ and G5-Fc₁₅ Alone. Higher activation voltages (-5 V) than aqueous

electrocuring (-2 V) is applied in organic electrocuring due to the higher resistance of the organic formulations. Electrocuring is monitored in three stages: 1) Voltage off, 0-2 min. 2) Voltage on, 2-48 min. 3) Voltage off, 48-50 min. The first stage retrieves reference viscosity and viscoelasticity of the uncured samples. The second stage records the real-time viscoelastic electrocuring properties and the third stage analyses for any continued polymerization propagation or relaxation by electric field removal. The storage moduli (G') and the loss moduli (G'') values of G5-Dz₃₀ and G5-Fc₁₅ conjugates are recorded as control (G5-PAMAM control is shown in **Figure S5a**) to compare with G5-Fc₁₅-Dz₃₀ conjugates, where the liquid to solid transition is shown in **Figure 2b (SI-Video2)**. With no voltage applied, G'' is greater than G' (liquid, viscous) with little to no drift for all samples as displayed in **Figure 2c** and **Figure S5c** (no voltage applied on G5-Fc₁₅-Dz₃₀ sample up to 40 min). Upon voltage activation, G5-Dz₃₀ displays little to no increase until 5 min of activation, with no observations of N₂ evolution. In terms of G5-Fc₁₅ conjugate, it exhibits a faster kinetics response to the applied voltage, raising about one order of magnitude in G' within 5 min. Crosslinking is speculated to be from H abstraction or free radical formation from amine-mediated electrochemical redox processes.^{14, 55-58} For cografed G5-Fc₁₅-Dz₃₀ conjugate, there is a two order-of-magnitude increase of G' and G'' values upon voltage activation with concurrent foaming (N₂ gas). G5-PAMAM controls display little to no crosslinking (**Figure S5a**). ¹⁹F NMR investigations exploit the -CF₃R group on the diazirine crosslinker to elucidate new covalent bonds on the carbene carbon. The ¹⁹F NMR data in **Figure S4** observes consumption of the aryl-diazirine-CF₃, but no new peaks are detected that would allow assignment of the crosslinking mechanism on the neighbouring -CF₃ carbene carbon. Any crosslinked samples appear to be insoluble and precipitate. This is visually confirmed in the NMR sample tubes. **Figure S4** displays less ¹⁹F intensity (with PF₆⁻ as internal standard) after extracting leachate from the Zensor® chip. Removing the voltage

gradient results in plateaued moduli with no further modulus changes. Gas bubbles from the G5-Fc₁₅-Dz₃₀ sample accumulate on the edges of the rheometer probe as seen in **Figure 2b** (SI-Video1). When removing the stainless steel rheometer probe, the crosslinked adhesive undergoes cohesive failure, as the organic gel fractures within the matrix, coating both the stainless steel probe and glassy carbon electrode as seen in **Figure 2b** (SI-Video2), indicating the interfacial adhesion is stronger on the metal and carbon/plastic surfaces than the bulk matrix crosslinking.

Figure 2. (a) Electrorheology schematic illustration. RE, reference electrode; WE, working electrode; CE, counter electrode; PP05, 5 mm probe, parallel-plate geometry; electric field demonstration is modelled by COMSOL software, 0.60 mm gap size is displayed as example. (b) Electrocure adhesive before and after curing. Gas evolution is visual observed. Cohesive failure causes probe/electrode fracture. (c) Real time dynamic mechanical analysis of G5-Dz₃₀, G5-Fc₁₅, and G5-Fc₁₅-Dz₃₀ adhesives. Storage modulus (G' , solid line) and loss

modulus (G'' , dot dashed line) throughout. Voltage off: 0-2 min. Voltage on: 2-48 min. Voltage off: 48-50 min. All conjugates formulations contain 0.1 M Bu_4NPF_6 as electrolyte. (d) Log G' comparison of G5-Dz₃₀ (grey), G5-Fc₁₅ (red), and G5-Fc₁₅-Dz₃₀ (blue) versus voltage time applied (all measurements were done in triplicate). (e) G' kinetics of G5-Dz₃₀ (grey), G5-Fc₁₅ (red), and G5-Fc₁₅-Dz₃₀ (blue) conjugates after 10 min voltage time applied.

Fc Grafting Catalyzes the Crosslinking of Electrocurable Adhesive. G5-PAMAM with Fc internal additives attempt to mediate the heterogeneous electron transfer reactions between the electrode and aryl diazirine grafted dendrimers, as well as enabling homogeneous electron transfer reactions between linked and non-linked grafted dendrimers. The storage modulus for G5-Dz₃₀, G5-Fc₁₅, and G5-Fc₁₅-Dz₃₀ conjugates are compared at 0, 1, 5, and 46 min in **Figure 2d**. At 0 min, all conjugates display similar viscoelastic liquid properties, where $G'' > G'$, and G' is ~ 1 -2 Pa. Without the internal conducting additive of Fc, G5-Dz₃₀ conjugate (grey columns) exhibit a sluggish increase of G' that is limited to 55 Pa (standard deviation, $\delta = \pm 10$ Pa) at 46 min. Similar moduli are observed with free, non-grafted Fc dissolved within G5-PAMAM/DMSO (data not shown). Comparing with G5-Dz₃₀ conjugate, G5-Fc₁₅ conjugate (red columns) exhibits a faster G' increase within 1 min but halts at a maximum 105 Pa ($\delta = \pm 25$ Pa) at 46 min. G5-Fc₁₅-Dz₃₀ conjugate (blue columns) has an exponential rise in kinetics within the first few minutes, but linearly increases thereafter to 3400 Pa ($\delta = \pm 500$ Pa) at 46 min. To compare the reaction rates as a function of time, G' kinetics are obtained through differentiation of the electrorheometry plots from **Figure 2c** and listed in **Figure 2e**. Both Fc grafted conjugates exhibit sharp peaks within 5 min voltage activation, indicating the activation of redox processes that lead to electric field alignment or crosslinking of conjugates, while the G5-Dz₃₀ requires a delay before any increase in storage

modulus is observed. This observation indicates that with grafting of Fc, redox reactions activate immediately upon voltage through the established electric field.

Leachate Evaluation Displays a Synergistic Mass Loss of G5-Fc₁₅-Dz_Y Matrix. The G5-PAMAM conjugates are evaluated before and after electrocuring to compare the soluble fractions (leachate) as a means to estimate insoluble intermolecular crosslinking, as seen in **Figure 3a-3b**. If little to no crosslinking occurs, then the major mass fraction will dissolve into neat DMSO after the potential is applied. If intermolecular covalent bonds are formed, the crosslinked matrix will be insoluble or filtered out (0.2 μ m) in the SEC sample preparation. After electrocuring, G5-PAMAM, G5-Dz₃₀, and G5-Fc₁₅ conjugates have greater than 70% mass retention as measured by the RI detector (**Figure 3a**). Quantitation of the grafted Fc and Dz by UV spectroscopy corroborate the retention of the conjugate's mass (**Figure 3b**). With no grafted Fc, G5-Dz₃₀ displays an 18% reduction of Dz, corroborating the rheometry results presented above and in **Figure 2c**. This is likely due to the diminished absorption coefficient from diazirine ($\epsilon_{353} = 266$) to reduced diaziridine ($\epsilon_{353} = 0$).⁵⁹ G5-Fc₁₅-Dz_Y conjugates display strong inverse correlations between percent Dz grafted and percent retained after electrocuring for dendrimer mass (Pearson's $r = -0.96$) and Dz mass (Pearson's $r = -0.99$), signifying that the higher the percent Dz grafted, the less that is retained after electrocuring. Less than 35% of conjugates mass is recovered after electrocuring and less than 50% of the grafted Dz is retained. The discrepancy between the two measurements likely results from residual UV absorbance of Fc grafting that remains after carbene crosslinking. Regardless, the ratio between uncured and cured UV absorbance (ABS) grows with increasing Dz grafting percentage.

Figure 3. (a) Refractive index (RI) analysis (area under curve) before (white) and after (grey) 46 min electrocuring (all measurements were done in triplicate). Refractive index is proportional to dendrimer mass. (b) ABS analysis (area under curve @ 360 nm) before (white) and after (grey) 46 min electrocuring (all measurements were done in triplicate). Absorbance is proportional to diazirine mass. (c) Comparison of G5-Fc₁₅-DZ₃₀ at a range of sample thickness. (d) Comparison of G5-Fc₁₅-DZ_Y gelation times from 2-8 min voltage applied. Storage modulus (G', solid line) and loss modulus (G'', dot dashed line) throughout. Voltage off: 0-2 min. Voltage on: 2-48 min. Voltage off: 48-50 min. All conjugates formulations contain 0.1 M Bu₄NPF₆ as electrolyte.

Electrocuring Kinetics and Mechanical Properties are Dependent on Sample Thickness. Gap size between the rheometer probe and Zensor® chip varies the sample thickness during the electrocuring measurements of G5-Fc₁₅-Dz₃₀ conjugates. Thus, the electric field between the working electrode and counter electrode is varied. The demonstration of electric field between probe and working electrode is displayed in **Figure 2a**. Applying Gauss's law ($\Phi_E = Q/\epsilon_0$, where Φ_E is the electric flux through a closed surface enclosing any volume, Q is the total charge enclosed within volume, ϵ_0 is the electric constant), the current density or charge flux will exponentially decrease as the sample thickness increases. If this relationship holds true in electrocuring kinetics, inhibition of adhesive crosslinking occurs furthest away from the electrodes — at the rheometer probe interface given the planar geometry of the two surface electrodes on Zensor® 3-electrode chip. Three sample thicknesses of 0.15, 0.30, and 0.60 mm are evaluated for G' and G'' with the fastest curing sample of G5-Fc₁₅-Dz₃₀ held at -5 V (**Figure 3c**). A strong linear correlation (Pearson's $r = 0.98$) exists between gelation time and sample thickness, and a linear inverse correlation (Pearson's $r = -0.93$) exists between gelation time and final G' values (**Figure S6b**). The fastest electrocuring kinetics is observed at 0.15 mm, which also has the highest G' . Sample thickness introduced an increasing curing latency across all samples, which is also observed in **Figure 3d** when Dz grafting is varied.

Crosslinking Kinetics of G5-Fc₁₅-Dz_y is Dependent on Grafting Percentage. The gelation time, defined where $G'' = G'$, is a simple measure of comparing crosslinking kinetics, where reduced time points indicate a faster transition from viscoelastic liquid to solid behaviour. Gelation times occurred at 6.3 min, 4.4 min, and 3.1 min, for G5-Fc₁₅-Dz₇, -Dz₁₅, and -Dz₃₀, conjugates respectively, as analysed in **Figure 3d**. The gelation time decreases with the increasing amount of grafted Dz on G5-PAMAM and the correlation falls into a strong inverse relationship (Pearson's $r = -0.96$, **Figure S6a**). The strong inverse

correlation of percent Dz vs. gelation time is consistent with the aqueous observations of -0.97 reported previously.¹⁴

Fc Cografted Conjugates Achieves Higher Storage Modulus in Organic Solvents than Aqueous Solvents. Electrocurving kinetics of several representative adhesive samples are compared in **Figure 4a**. G5-Fc₁₅ and G5-Fc₁₅-Dz_Y conjugates are aqueous insoluble therefore not available for aqueous electrocuring comparisons (Fc-containing conjugates are only soluble at low concentration, 2 mg/mL, acidic mediums). G5-Dz₃₀ conjugates achieves ~1000 Pa storage modulus when electrocured in aqueous solvents (1X PBS buffer as electrolyte). For comparison, G5-Dz₁₅ data is replotted from previous report¹⁴ with concentration of 25 wt% in 1X PBS. The G' values reach over 80% of their maximum values after only 1-min voltage activation, and achieve G' values of 1000 ± 80 Pa. The G5-Dz₃₀ conjugate exhibits a more inert response when electrocured in DMSO. Compared to G5-Dz₃₀, the G5-Fc₁₅-Dz₃₀ conjugate increases at a slower rate with an achieved G' value of 300 ± 50 Pa after 5-min voltage applied. The advantages of non-aqueous electrocuring allows extended curing times without the electrolysis reactions involved in aqueous solvent. With the extended voltage stimulus, a final G' value of 3400 ± 500 Pa after 46-min is attained. Furthermore, Fc cografted conjugates are found electrocuring in DMF and polyethyleneglycol-400 (PEG400) (which serve as organic solvents with low dielectric constants: 37 and 16⁶⁰, respectively) as well (**Figure 4a** and **Figure S5b**): final G' values achieve 500 ± 50 Pa in DMF and 200 ± 30 Pa in PEG400 with 25 wt% concentration of G5-Fc₁₅-Dz₁₅ conjugates. And both solvents display viscous (liquid) properties before curing, with electrocuring gelation times similar to DMSO.

Peroxide Additives are Not Required for Eletrocuring. Moreover, to challenge the hypothesis that additional oxidants are required for carbene formation,²² two organic peroxide additives, either urea peroxide (UPO) or benzoyl peroxide (BPO) are added to the

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3 formulation. This serves to replace the anodic oxidants created by water electrolysis, which is
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5 theorized to aid in carbene formation of the aqueous formulations. The electrocuring kinetics
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7 is compared by monitoring the G' values at three time points upon voltage application
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9 (**Figure S7**): 0 (initial), 1, 5, and 46 min. Addition of UPO or BPO into G5-Dz₃₀ and G5-
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11 Fc₁₅-D_Y samples leads to no improvement in kinetic rates or modulus values when compared
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13 with no-peroxide control (**Figure S7a**). Increasing molar ratios of UPO to G5-Fc₁₅-Dz₃₀ are
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15 observed to hinder the 1 min kinetics, but no consistent correlations are noted after 5 or 46
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17 min (**Figure S7b**).
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20 **Tack Adhesion Strength Correlates with Diazirine Grafting.** Tack adhesion evaluates
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22 the electrocured formulations through tensile normal forces (F_N). **Figure 4b** displays the
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24 maximum tack adhesion strength (normal stress at failure) of all adhesive formulations,
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26 comparing with control samples: G5-PAMAM, G5-Dz₃₀, and G5-Fc₁₅, respectively. The
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28 control samples display 2.5 N/cm², which is same as the formulations without applying any
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30 voltage as seen in **Figure 4b**. Cograftered G5-Fc₁₅-Dz_Y conjugates exhibit an obvious increase
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32 of tack adhesion strength, especially for G5-Fc₁₅-Dz₃₀. A strong linear correlation of tack
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34 adhesion strength and Dz conjugate with a linear fit of Pearson's $r = 0.985$ is displayed,
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36 indicating that the adhesion strength is tunable as a function of Dz grafting.
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Figure 4. (a) G' values of electrocuring formulations: G5-Dz₃₀ and G5-Dz₁₅ conjugates in aqueous solution (1X PBS, at -3 V and -2 V voltage activation, respectively) vs. G5-Dz₃₀, G5-Fc₁₅, and G5-Fc₁₅-Dz₃₀ conjugates in DMSO and G5-Fc₁₅-Dz₁₅ conjugates in DMF and PEG400, at -5 V voltage activation. * G5-Dz₁₅ conjugates is replotted from reference, the concentration of G5-Dz₁₅ conjugates is 25 wt% in PBS. G5-Fc₁₅ and G5-Fc₁₅-Dz_Y conjugates are insoluble in PBS, pH 7.4. (b) Tack adhesion of electrocured formulations (grey columns) and uncured control (white columns). Significant differences are indicated by *p < 0.05, no significant difference is indicated by NS. All measurements were done in triplicate.

G5-Fc₁₅-Dz_Y Has Irreversible Dz Reduction with Reversible Fc Oxidation. Quasi-reversible behaviour is observed for aryl diazirine in DMSO, but in the presence of 1.0% acetic acid (acting as the proton donor)^{14, 20}, the aryl diazirine is chemically irreversibly reduced to aryl diaziridine in **Figure 5a**. The cyclic voltammograms of G5-Dz₁₅ conjugate retain the properties of free aryl diazirine: in the absence of the acetic acid, G5-Dz₁₅ conjugate has quasi-reversible redox behaviour; with the addition of acetic acid, only the reduction peak for the conjugate is observed in **Figure 5b**. Redox potentials of all samples are listed in **Table S2**, vs. Ag/AgCl (saturated LiCl in ethanol). Free Dz (aryl diazirine) compared to dendrimer grafted Dz (G5-Dz₁₅) in the absence of acid shows a positive shift in reduction potential (E_{pc} , from -1.6 to -1.25) and displays a negative shift in its oxidation potential (E_{pa} , from -1.0 to -1.1) when the scan direction is reversed so that the reduced form is oxidized back to the starting material. Overall, this results in a decreased value of peak separation ($\Delta E_p = E_{pa} - E_{pc}$) of 0.45 V. ΔE_p values between free Dz and grafted Dz, indicate less electromotive force is required to create the diazirinyl radical, but with more reductive potential for grafted Dz. Free Fc and G5-Fc₁₅ in **Figure S9b-S9c** displays an opposite trend—more electromotive force is required to oxidize grafted Fc, ultimately creating ferrocenium (Fc^+) that has a higher oxidation potential with ΔE_p values ranging from 0.28 to 0.16.

G5-Fc₁₅-Dz_Y cyclic voltammograms are tested without the presence of acetic acid in **Figure 5c**. Peaks are observed for Fc in the range of 0.20 V to 0.80 V and Dz in the range of -1.20 V to -1.60 V. Peak intensity of Dz rises with increasing Dz grafting. No oxidation peaks for Dz grafting is observed, indicating the redox behavior became chemically irreversible with the grafting of Fc. Fc is not a proton donor, but is a source of electrons, and Fc^+ serves as a hole charge carrier and potential oxidant. The ΔE_p of Fc in G5-Fc₁₅-Dz₃₀ is 0.17 V wider than the rest of cogenerated conjugates, which corresponds to the doubling of Dz grafting. ~~Additional diazirinyl generation appears to influence the redox behaviour of Fc.~~

The quasi-reversible electrochemical reaction is exhibited in **Figure S10**, and the proposed voltage-activated crosslinking reactions are depicted in **Figure 5d-5e**. There are three possibilities for carbene to form the crosslinking: (1) insert to amide groups and (2) insert to amine groups of G5-PAMAM, or (3) self-crosslink to form azine. For conjugates samples, the current signals decay after three cycles as seen in **Figure S9**. Possible explanations include electrode grafting or amine oxidation.^{55-58, 61-63}

Figure 5. Electrochemical behavior of: (a) Aryl diazirine and (b) G5-Dz₁₅ conjugates in the absence (solid line) and presence of 1.0% acetic acid proton donor (dot dashed line). (c) G5-Fc₁₅ and G5-Fc₁₅-Dz_Y conjugates. All cyclic voltammograms were recorded in DMSO containing 0.1 M Bu₄NPF₆ as electrolyte at glassy carbon electrode (d = 3 mm). Scan rate: 100 mV/s. (d) Possible crosslinking reactions between diazirine ($\rightarrow$ carbene) and G5-PAMAM dendrimers. (e) Simplified scheme for depicting the proposed hole conduction and carbene activation.

DISCUSSION

Fc and Dz Dendrimer Cografts Enable Electro curing in DMSO. For the first time, a model system is demonstrated towards the development of voltage-activated crosslinking adhesives in a water-free environment. Structure activity relationships of fifth generation polyamidoamine (G5-PAMAM, 30 kDa) grafted with diazirine (Dz, a carbene precursor) and ferrocene (Fc, an internal conductive additive) were applied towards an electro curing adhesive in DMSO organic solvent. Chemically irreversible reduction was only possible with Fc and Dz co-grafting, with an observed synergistic rise in storage modulus compared to either grafted carbene precursor or internal additive alone. G5-Fc₁₅-Dz_Y (Y=7%, 15%, and 30%) conjugates exhibited liquid properties and crosslinked to a viscoelastic solid within minutes of low voltage excitation, which are hallmarks of an ideal one-pot event activated adhesive. Strong correlations were observed with respect to Dz grafting ratio on cured modulus and gelation time, which provides a pathway for tunable mechanical and adhesive properties. Variations in electric field and gap thickness (**Figure 2a** and **Figure 3c**) displayed similar correlations on electro cured modulus and a kinetic latency time. Additional oxidants were not required and did not serve to increase storage modulus kinetics or cured storage modulus. Fc grafting induces irreversible grafted Dz reduction and Dz shifts the redox properties of grafted Fc.

The previous investigation of aqueous electro curing of PAMAM-g-diazirine,¹⁴ attempted to replicate the voltage activated crosslinking in organic solvents (*e.g.* acetonitrile) with no success, but with the caveat that the diazirine (-N=N-) had been reduced to the diaziridine (HN-NH), while subsequent oxidation of diaziridine to carbene failed. This may be attributed to lack of catalyst to activate the diaziridine into carbene. When G5-Dz₃₀ was electroactivated in DMSO, a measureable increase in G' was detected, but SEC indicates little to no crosslinking — dendrimer mass and diazirine concentration remained approximately the same (**Figure 3a-3b**). Similar result was observed in ¹⁹F NMR

examinations for before and after G5-Dz₃₀ electrocuring: the intensity of -CF₃ from Dz units change less than 8% (**Figure S4c-S4d**). The G' increase may result from attractive hydrogen bonding or electrostatic attraction of diazirinyl/amine. G5-Fc₁₅ conjugates displayed a rapid G' response upon the voltage application that was similarly found to have little to no crosslinking by SEC. Electrooxidation to PAMAM-g-ferrocenium may lead to electrostatic or redox mediated aggregations (*e.g.* Fc⁺-electrolyte bridges), forming reversible non-covalent bonds as seen in other Fc grafted polymers.^{64, 65}

Enhanced Charge Transport of Redox Dendrimer and Hole Network Activated Carbene Crosslinking. Due to the kDa molar masses of G5-PAMAM conjugates ($M_w > 30$ kDa) its improbable for PAMAM dendrimers to diffuse from the cathode to the anode (~ 0.1 mm apart) at these time scales. We postulated that the carbene crosslinking observed in the DMSO is attributed to two supporting mechanisms: the enhanced charge transport of redox dendrimers and the immobilized donor-acceptor network created through Fc/Fc⁺ oxidation and Dz/Dz⁻ reduction^{66, 67}. The rapidly created donor-acceptor network allows the electron transduction across the bulk matrix. With the Fc cografted on the conjugates, Dz is irreversibly reduced to diaziridine without the proton donors, suggesting that Fc/Fc⁺ acted as the hole transfer carrier for electron hopping and its redox property allowed it to be cyclically regenerated. Our system exploited Fc's unique behaviour when grafted to dendrimers. Fc-grafted onto self-assembled monolayers results in multiple redox peaks attributed to varying electrolyte micro-environments.⁶⁸ However, when Fc is grafted on dendrimers, the multiple redox centers appear as a single but broad redox peak (**Figure 5c**).⁶⁷ Once the voltage was activated, Fc-Dz units were converted to Fc⁺-Dz⁻, preparing donor-acceptor charge transfer zones and rapidly creating a conductive network within minutes (**Figure 5e**). We speculated that the rise in resistance over time was due to the charge imbalance caused by the conversion of negatively charged diazirinyl radical to carbene, which is formed on electron reduction of

Dz ($\text{Fc} + \text{Dz} \rightarrow \text{Fc}^+ + \text{Dz}^- \rightarrow \text{Fc}^+ + \text{carbene}$). Diazirinyll is a strong reductant with a relatively long lifetime ($t_{1/2} = 46 \text{ s @ } 10^\circ\text{C}$) which can donate an electron to Fc^+ or other adjacent diazirines.²¹ The electron conduction between cathode and anode was made possible by dendrimer grafted Fc (but not free Fc). The addition of the oxidants urea peroxide and benzoyl peroxide to G5-Dz or G5-Fc₁₅-Dz_Y had no discernible effect on storage modulus, suggesting that diaziridine may not be the carbene forming intermediate. This implies that the rate limiting reaction is then the reductive diazirinyll radical to carbene via an unknown mechanism. Indirect observations support the statements above: higher grafting Dz ratios decrease $\text{Dz}^- - \text{Fc}^+$ distances, increasing instantaneous electron transduction with a corresponding decrease in gelation time (**Figure 3d**). As the Dz^- are converted to functional groups (*e.g.* carbene, azine) with reduced charge transfer, resistance rises and current drops over time (**Figure S8**). Diminishing electric field (**Figure 2a**) will have a direct effect on the kinetics of electron hopping (*vs.* spontaneous propagation), which was observed with increasing sample thickness between the working electrode and rheometer probe (**Figure 3c**). The mechanism of intermolecular dendrimer crosslinking is likely to be a complex mixture of carbene (C-H or N-H) insertion and azine crosslinking.^{69, 70} The mechanism of crosslinking allowed adhesion on both stainless steel (rheometer probe) and polypropylene/glass carbon substrate (Zensor® chip electrode) — cohesive failure coated a layer of adhesive on both substrates when separated (**Figure 2b**). Metallocenes other than ferrocene may improve the hole network properties in organic electrocuring. Cobaltocenium for example has a much lower oxidation voltage (-1.3V compared to Fc/Fc^+), but is relatively unstable in air and moisture environments.^{71, 72} While cobaltocenium as an 18-electron cationic metallocene is a desirable candidate for hole carrier.⁷³⁻⁷⁵ Other redox centers, such as nitroxyl, phenoxyl, carbazol, quinones, viologens, and hydrazyl, are also possible to balance the donor-acceptor charge transfer to modify Dz grafted adhesives⁴². Future work will address suitable redox

mediators applicable to redox active gels to further improve the electron transduction efficiency and lower the time-dependent resistance⁷⁶.

The simple two-step synthetic strategy was designed to prevent Fc and Dz cografting on one terminal amine. Investigations by 2D NMR analysis (**Figure S3**) found no evidence of disubstituted amines with Fc and Dz, although previous investigation of high ratios (20-30%) of diazirine grafting yielded disubstituted amines, which cannot be rule out herein.¹³ The theoretical spacing between Fc and Dz sites is less than 2 nm at the 22-45% grafting (based on n=120 polyhedron, 5.4 nm diameter). The spherical nature of PAMAM dendrimers allowed the adhesive formulation to achieve a high concentration while maintaining viscous flowable properties ($G'' > G'$). With 50 wt% concentration (maximum concentration in DMSO), dendrimer conjugates are considered 'random closely packed', which is favourable to intermolecular covalent bonding.⁷⁷ Both intermolecular and intramolecular electron transfer was aided between redox active sites and working electrodes by electron tunneling, which is facilitated by dendrimer networks.^{14, 78-80}

G5-Fc₁₅-Dz_Y Conjugates Motivated by Donor-Acceptor Pairs in Metal Organic Frameworks (MOFs). The electrocuring adhesive formulations herein have donor-acceptor concentrations over $10E+20 \text{ cm}^{-3}$ which meets the high charge density requirement of metal organic frameworks, (MOFs, $>10E+15 \text{ cm}^{-3}$)⁸¹. The conductive mechanisms of MOFs rely on long range charge transport pathways through electron hopping or band transport. The choice of internal additives attempts to mimic the donor-acceptor mechanisms known in MOFs, where ferrocene serves as the metal ion and diazirine as the organic linker, albeit in a non-coordinated, dynamic liquid. Similar to MOFs, the design of metal ion and organic linker will influence the conductive properties, which is part of our future work. The energy diagram (**Figure S12**) for Fc^+/Dz^- diluted in DMSO/electrolyte displays a $2.0 \pm 0.1 \text{ eV}$ band gap. It is unknown if the charge transport is predominantly intermolecular or intramolecular,

hence further exploration on cograftering vs. mixing is required. Many donors (*e.g.* naphthalene, perylene, and tetrathiafulvalene) and acceptors (*e.g.* tetracyanoethylene, fullerene, quinone, and pyromellitic dianhydride)⁸² are known, and will require optimization of donor-acceptor ratios to yield high crosslinking moduli and complete Dz/crosslinker consumption.

Benefits of Organic vs. Aqueous Electro curing. Selection of DMSO as solvent serves as a model system towards transitioning from aqueous to organic environment. Organic formulations allow higher activation voltage (-5 V) than aqueous (*i.e.*, -2 V), with the additional benefits of higher concentration, viscous properties, and higher storage modulus upon electro curing. Aqueous electro curing requires the lowest voltage possible due to competing electrolysis. One of the most important differences between organic and aqueous electro curing was the decrease in gas generation and subsequent foaming by H₂ and O₂, while DMSO solvent has only N₂ as a gaseous by-product (**Figure 1a**). The gelation time points of DMSO were comparable to aqueous (both 3-6 min) but the final G' values are 4-5 times higher, due to longer durations of voltage activation made possible by preventing water electrolysis. However, the G' values are still a fraction of what is achievable by photocured PAMAM-g-diazirines.^{13, 83} This is in part due to the plastization by DMSO and incomplete crosslinking due to the decreasing current migration over time (**Figure S8**). Storage modulus may be improved through a number of techniques. For example, choice of oligomer/ionic solvents, incorporating oxidative crosslinking and optimized electrolyte mediators, which will be the focus of our future work. DMSO is a common plasticizer for bioerodible polymers (*e.g.* poly(lactic-co-glycolic acid), PLGA, with MPa shear modulus) that become viscous liquids when dissolved at 50-60% DMSO.⁸⁴⁻⁸⁶ DMSO is commonly employed for in situ drug depots because of its many advantages: one of the lowest levels of tissue toxicity among suitable depot solvents, reduces burst release, completely miscible with water, and dissolves a

range of drugs (lysozyme protein, cisplatin inorganic, hydrophobic risperidone) and bioerodible polyesters.⁸⁶⁻⁹⁰ One of the drawbacks of in situ implants is their lack of reproducible depot shape, which could be directly alleviated with the electrocuring principles presented herein.⁸⁸ PEG400's low toxicity is exploited for a wide range of purposes including cosmetics, cryogenics, drug depots, and solvent extraction.⁹¹⁻⁹³ Besides DMF and PEG400, other aprotic solvents such as dimethyl carbonate, propylene carbonate, 1-methyl-2-pyrrolidone, are also possible for a combination of drug depot and organic electrocuring due to their biocompatible properties.⁹⁴⁻⁹⁷

Immobilization of Biosensors and Nanobatteries Based on Dendrimer-Fc Conjugates. Fc and Dz were previously linked together as a small molecule conjugate to functionalize graphene and carbon nanotube surfaces.⁹⁸⁻¹⁰⁰ Dz was exploited for its photocuring carbene crosslinking to label Fc on the carbon allotrope, whose redox behaviour served to characterize the surface modification on the conductive electrodes. Dendrimer Fc conjugates structures have been applied towards anion and cation sensing, detection of specific oligonucleotides, molecular nanobatteries, and surface redox investigations.^{48-51, 67, 71, 101-104} The stimuli-sensitive feature of Fc combined with the tailorable and easily-grafted dendrimer architecture allows electrochemical approaches not possible with other designs. Our results demonstrated how one-step grafting of aryl-diazirine to dendrimer-Fc conjugates may allow voltage activated immobilization, expanding the dendrimer-metallocene application window on to sensitive substrates and into new environments where thermo- and photo-curing methods have prevented application. Moreover, DMSO's miscibility with both aqueous and organic solvents allows ease of extraction after matrix crosslinking enabling the possibility of both flexible electronics, implantable biosensors, and current activated drug depots, which will be explored in our future work.

▪ CONCLUSIONS

A series of voltage-activated adhesive dendrimers with donor-acceptor internal additives was developed towards a model system for one-pot adhesives. DMSO, DMF, and PEG400 were found to act as a suitable solvent for electrocuring that avoided electrolysis gaseous by-products, allowing extended times (up to 45 min) of voltage curing not possible in aqueous solutions. Electrorheology measurements employing relatively high voltages of -5 V activated conductive $\text{Fc}^+ \text{-Dz}^-$ organogel networks in insulating solvents. The conductive milliamperic current carrying network activates carbene insertion crosslinking. The one-pot electrocuring adhesive allows application on opaque and thermally sensitive substrates under ambient conditions, opening new applications in flexible electronics, implantable biosensors, and adhesive drug depots.

▪ ASSOCIATED CONTENT

Supporting Information. Quantitation of Fc and Dz dendrimer grafting, including ^1H NMR spectrum and SEC-MALS-UV spectrum; 2D NMR of $\text{G5-Fc}_{15}\text{-Dz}_{30}$ analysis; ^{19}F NMR analysis of before and after electrocuring adhesive formulations; Electrorheology results of G5-PAMAM and $\text{G5-Fc}_{15}\text{-Dz}_{30}$ as control, and $\text{G5-Fc}_{15}\text{-Dz}_{15}$ electrocuring in DMF and PEG400 solvents; Linear correlations in $\text{G5-Fc}_{15}\text{-Dz}_Y$ crosslinking kinetics studies; Adhesive formulations electrocuring in the presence of peroxide additives; Current and resistance of formulations measured in electrorheology; CV scanning for G5-Fc_{15} conjugates; Quasi-reversible electron transfer path in CV scanning; UV absorbance spectra of conjugates with summary of the UV coefficient values; Energy diagram of Fc and Dz in conjugates; Videos of electrorheology testing, are supplied as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing interests.

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TOC graphic

88x34mm (300 x 300 DPI)

Figure 1. (a) Scheme of electrocuring in aqueous vs. organic solvents. Aqueous solutions liberate hydrogen and oxygen gases, causing excessive foaming. (b) Synthetic route of intermediate conjugates, G5-FcX (X = 15%), and cograftered conjugates, G5-FcX-DzY (X = 15%, Y = 7%, 15%, 30%).

165x140mm (300 x 300 DPI)

Figure 2. (a) Electrorheology schematic illustration. RE, reference electrode; WE, working electrode; CE, counter electrode; PP05, 5 mm probe, parallel-plate geometry; electric field demonstration is modelled by COMSOL software, 0.60 mm gap size is displayed as example. (b) Electrocure adhesive before and after curing. Gas evolution is visual observed. Cohesive failure causes probe/electrode fracture. (c) Real time dynamic mechanical analysis of G5-Dz30, G5-Fc15, and G5-Fc15-Dz30 adhesives. Storage modulus (G' , solid line) and loss modulus (G'' , dot dashed line) throughout. Voltage off: 0-2 min. Voltage on: 2-48 min. Voltage off: 48-50 min. All conjugates formulations contain 0.1 M Bu4NPF6 as electrolyte. (d) Log G' comparison of G5-Dz30 (grey), G5-Fc15 (red), and G5-Fc15-Dz30 (blue) versus voltage time applied (all measurements were done in triplicate). (e) G' kinetics of G5-Dz30 (grey), G5-Fc15 (red), and G5-Fc15-Dz30 (blue) conjugates after 10 min voltage time applied.

165x108mm (300 x 300 DPI)

Figure 3. (a) Refractive index (RI) analysis (area under curve) before (white) and after (grey) 46 min electrocuring (all measurements were done in triplicate). Refractive index is proportional to dendrimer mass. (b) ABS analysis (area under curve @ 360 nm) before (white) and after (grey) 46 min electrocuring (all measurements were done in triplicate). Absorbance is proportional to diazirine mass. (c) Comparison of G5-Fc₁₅-Dz₃₀ at a range of sample thickness. (d) Comparison of G5-Fc₁₅-Dz_Y gelation times from 2-8 min voltage applied. Storage modulus (G', solid line) and loss modulus (G'', dot dashed line) throughout. Voltage off: 0-2 min. Voltage on: 2-48 min. Voltage off: 48-50 min. All conjugates formulations contain 0.1 M Bu₄NPF₆ as electrolyte.

165x143mm (300 x 300 DPI)

Figure 4. (a) G' values of electrocuring formulations: G5-Dz30 and G5-Dz15 conjugates in aqueous solution (1X PBS, at -3 V and -2 V voltage activation, respectively) vs. G5-Dz30, G5-Fc15, and G5-Fc15-Dz30 conjugates in DMSO and G5-Fc15-Dz15 conjugates in DMF and PEG400, at -5 V voltage activation. *G5-Dz15 conjugates is replotted from reference, the concentration of G5-Dz15 conjugates is 25 wt% in PBS. G5-Fc15 and G5-Fc15-DzY conjugates are insoluble in PBS, pH 7.4. (b) Tack adhesion of electrocured formulations (grey columns) and uncured control (white columns). Significant differences are indicated by * $p < 0.05$, no significant difference is indicated by NS. All measurements were done in triplicate.

82x166mm (300 x 300 DPI)

Figure 5. Electrochemical behavior of: (a) Aryl diazirine and (b) G5-Dz15 conjugates in the absence (solid line) and presence of 1.0% acetic acid proton donor (dot dashed line). (c) G5-Fc15 and G5-Fc15-DzY conjugates. All cyclic voltammograms were recorded in DMSO containing 0.1 M Bu4NPF6 as electrolyte at glassy carbon electrode ($d = 3 \text{ mm}$). Scan rate: 100 mV/s. (d) Possible crosslinking reactions between diazirine ($\diamond$ carbene) and G5-PAMAM dendrimers. (e) Simplified scheme for depicting the proposed hole conduction and carbene activation.

165x98mm (300 x 300 DPI)