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Redox-Driven Framework Expansion in Viologen COFs for Programmable Electrochemical Actuation

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Abstract

Electrochemically driven ionic actuators operating at low voltages are promising for soft robotics, haptic interfaces, and adaptive systems. Yet, achieving fast response, large strain, long-term durability, and discrete stepwise actuation remains challenging. Here, we report a high-performance ion-driven actuator based on a viologen-based cationic covalent organic framework (V-COF), which integrates the ordered porosity and mechanical robustness of COFs with the rapid and reversible redox chemistry of viologen. The incorporation redox-active centers within the COF backbone enables redox-state-dependent lattice expansion and counterion diffusion under a small electrical bias, thereby translating molecular redox switching into controllable electrochemical actuation. The actuator exhibits a peak-to-peak bending strain of 1.86%, fast response time of 2.8 s, and cycling stability of 10,000 cycles with negligible degradation. Ex-situ and in-situ electrochemical analyses reveal that actuation is driven by reversible viologen redox reactions coupled with counterion diffusion through the ionically charged COF framework. This work establishes redox-active ionic COFs as a new class of actuator materials that bridge molecular-scale charge transfer and macroscopic motion, offering a new molecular design strategy for durable, low-voltage electrochemical actuation in soft robotic and smart-system applications.

1. Introduction

Actuators are devices that convert various forms of stimuli, such as thermal, chemical, pneumatic, electric, into mechanical motion, enabling dynamic control in systems ranging from soft robotics to artificial muscles.[1,2,3,4] Among these, electrochemical actuators (ECAs), also known as ionic actuators, have emerged as a particularly promising class owing to their ability to operate efficiently at low voltages (typically < 5 V) while offering soft, lightweight, and flexible motion.[5] The actuation in ECAs originates from volume or strain changes of the electrode materials, which occur through ion insertion and extraction processes, or from dimensional changes in conjugated polymers driven by redox reactions. Therefore, the choice and design of active materials play a decisive role in governing actuation performance. Over the past decades, wide range of materials such as 2D nanosheets,[6] MXene,[7,8,9,10] conjugated polymers,[11,12] carbon-based materials,[13,14,15] liquid metal [16] have been explored. However, a major obstacle persists in the development of ECAs that simultaneously achieve high electro-mechanical energy conversion efficiency, large output force, fast response time, and well-defined stepwise actuation.

Covalent organic frameworks (COFs) have emerged as a promising class of materials for ECAs, owing to their high accessible surface area that enables rapid ion transport and their structurally robust yet tuneable architectures.[17] Recent studies have demonstrated that electron-rich π-conjugated COFs enabled ultralow-voltage actuation without back-relaxation by providing polarized nanochannels that enable stress-free rapid ion migration.[18] Building on this concept, ionic COFs were subsequently developed through the incorporation of sulfonate ($-SO_3^-$) groups, either directly via functionalized

monomers or through post-synthetic modification, to further enhance ionic conductivity, capacitance and actuation performance.[19,20] More recently, electronically conjugated covalent triazine frameworks (CTFs) were integrated with MXene, resulting in synergistic hybrid electrodes that simultaneously enhanced electrical conductivity and expanded the ion-accessible active surface area.[21,22] However, in most prior studies of COF-based actuators, COFs were employed only as minor additives (< 10 wt%) within poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) electrodes, making it difficult to elucidate the role of COFs in electrochemical actuation. Moreover, COFs implemented in ECAs have mainly been explored as heteroatom-rich porous additives, ionic COF electrolytes, or ion-host frameworks, with their roles largely associated with enhanced ion transport, charge storage, and electrolyte–electrode interactions. To the best of our knowledge, the use of a COF as a primary redox-active framework, where built-in molecular redox centers directly couple charge compensation, ion migration, and electrochemical-ionic actuation, remains unexplored.

In this work, a 2D viologen-based cationic COF (V-COF) is prepared by Schiff-base polycondensation reaction between 1,1'-bis(4-aminophenyl)-[4,4'-bipyridine]-1,1'-diium chloride (V-NH_2) and 2,4,6-triformylphloroglucinol (TFG). Viologen, i.e., 4,4’-bipyridinium ions, is incorporated into the V-COF to impart redox activity through their well-known two-step reduction process ($V^{2+} \rightarrow V^{\bullet+} \rightarrow V^0$).[23] Viologen units endow V-COF with intrinsic redox activity, enabling efficient charge storage and reversible ion diffusion within the ordered 2D structure, thereby allowing the V-COF to function as the primary active component in ECAs. Furthermore, unlike majority of COFs synthesized with neutral building blocks, positively charged building blocks allow for stronger electrostatic forces for host-guest recognition.[24] The resulting V-COF electrode-based ECA exhibits a high peak-to-peak bending strain 1.86% at ±2.5 V, with good responsiveness in high frequency (5 Hz), and high blocking force up to 49.6 times its own weight. It also shows high stability, with maintaining 129.1% of its original displacement after 10000 cycles. The operating mechanism of the V-COF-based electrode, governed by the redox reaction of viologen, was elucidated through comprehensive ex-situ and in-situ electrochemical characterizations. Finally, V-COF-based ECA was successfully demonstrated in soft robotic gripper and two legged-crawler applications. This work establishes redox engineering of COFs as a promising strategy for next-generation ECA, enabling built-in redox centers to translate electrochemical switching into ion-coupled mechanical deformation.

2. Results

2.1 Synthesis and Characterization V-COFs

Amino-functionalized viologen (V-NH_2) monomer was synthesized based on previous literature via Zincke reaction **(Supplementary Methods, Figure S1)**.[25] Subsequently, V-COF was synthesized by imine polycondensation reaction between V-NH_2 and TFG **(**Fig. 1a**)**. Initially, the synthesis of V-COF was carried out using 6 M acetic acid (AA) as the catalyst. The formation of V-COF is supported by the emergence of the low-angle reflection at ~ 4.1°, assigned to the in-plane (200) reflection **(**Fig. 1c**)**.[26] However, several

additional reflections are observed between 12° and 30° that cannot be assigned to the expected simulated COF pattern. Because these features are relatively sharp and distributed over a broad high-angle region, they are unlikely to originate solely from the typical interlayer stacking reflection of a 2D COF. Instead, they may arise from residual crystalline molecular species or side products associated with the Zincke reaction, trapped ionic/counterion-containing domains, or a minor secondary ordered phase formed during polymerization. To further investigate this issue, synthesis with different AA concentrations (3 M, and 12 M) were also attempted, but the same additional peaks appeared. Notably, for V-COF synthesized with 12 M AA, the (200) peak disappeared while the other peaks remaining, suggesting the formation of an amorphous product resulting from incomplete imine condensation under strongly acidic conditions. Since 2017, Lewis acid catalysts, such as scandium triflate ($Sc(OTf)_3$) have been introduced in COF synthesis and shown to afford superior crystallinity and structural order compared to AA-synthesized COFs.[27] Inspired by these works, V-COF was synthesized with $Sc(OTf)_3$, which yielded V-COF with improved crystallinity, porosity and the absence of peaks associated with incomplete reactions observed in AA-synthesized V-COFs **(**Fig. 1c**)**. Therefore, $Sc(OTf)_3$ was chosen as the catalyst for subsequent results.

The successful reaction between V-NH_2 and TFG was further confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) **(Figure S2a)**. The disappearance of the characteristic C = O stretching band at 1638 cm^{-1} and the appearance of broad characteristic peak of the bipyridinium group at around 3000–3500 cm^{-1} indicated the complete formation of V-COF. More importantly, the ATR-FTIR spectra of V-COFs synthesized with 6 M AA and $Sc(OTf)_3$ were identical, confirming that the same chemical bonding was obtained regardless of the catalyst used **(Figure S2b)**. ^{13}C nuclear magnetic resonance (NMR) spectroscopy revealed that the resulting V-COF remains as enol form, as evidenced by the absence of a C = O peak typically observed in the 170–180 ppm region, indicating that keto-enol tautomerization to the keto form did not occur **(Figure S3)**. Brunauer-Emmet-Teller (BET) surface areas for the V-COF synthesized with 6 M AA and $Sc(OTf)_3$ were calculated within the P/P_0 range of 0.05 to 0.30, which were 161.31 and 472.69 m^2/g. $Sc(OTf)_3$-synthesized V-COF exhibited significantly higher porosity, indicating a higher degree of structural order than the 6 M AA synthesized V-COF.[24,28] Pore size distributions were derived using nonlocal density functional theory (NLDFT), but due to pore blockage, no well-defined pore size distribution was obtained.[24] Nevertheless, V-COF was concluded to exhibit porosity in the micro- to mesoporous range. Due to its cationic nature, V-COF was intrinsically hydroscopic, as around 15 wt% weight loss was attributable to water evaporation below 100°C **(Figure S5)**. Framework degradation occurred with the weight loss around 250°C, as indicated by the associated weight loss. The low degradation temperature was likely the result of V-COF remaining in the enol form rather than the more stable keto form. The scanning electron microscope (SEM) images of synthesized V-COFs show a rod-shaped morphology **(**Fig. 1d**)**. Powder X-ray diffraction (PXRD) revealed peaks at approximately 2.2° and 4.4°, corresponding to the (100) and (200) Bragg reflections of a hexagonal lattice with unit-cell parameters a = b = 4.45 nm (Fig. 1b). These peaks are in good agreement with the simulation results and previous reports. **(Figure S6, S7)**.[26,29] The transmission

electron microscope (TEM) image clearly showed parallel lines with an adjacent distance of around 4.65 Å, which is attributed to the stacking structure around the *c*-axis of the of the V-COFs **(Figure S8)**. The relatively large stacking distance was likely due to the cationic repulsion between the bipyridinium moieties. The combination of enhanced porosity achieved through optimized synthesis conditions and expanded interlayer spacing renders V-COF a promising electrode material for efficient ion diffusion ionic actuator applications.

2.2 Fabrication of V-COF:CNT Membranes

As V-COF was electrically insulating, single-walled carbon nanotubes (CNTs) were selected as the composite component owing to their excellent mechanical strength, high electrical conductivity, and good chemical stability.[15] Initially, PEDOT:PSS was also investigated, as it is a widely used conjugated polymer electrode material for COF-based ionic actuators and it readily formed a free-standing membrane. However, it was difficult to independently assess the individual contributions of V-COF in the PEDOT:PPS composite-based actuators. The V-COF:CNT composite membrane was fabricated by two-step dispersion process. When V-COF and CNT were sonicated together from bulk, V-COF did not disperse properly due to strong π-π interaction with the surface of CNTs **(**Fig. 2a**)**. Therefore, V-COF and CNT were first dispersed separately by probe sonication in deionised water, using Triton X-100 as the surfactant in both cases. The two dispersions were then combined and further homogenzied by probe sonication. Finally, the resulting mixture was deposited onto a polyvinylidene fluoride (PVDF) filter by vacuum filtration to form a free-standing membrane **(**Fig. 2b**)**. The crystallinity of V-COF was retained after the sonication and membrane fabrication processes, as confirmed by XRD analysis **(Figure S9)**.

To optimize the weight ratio between V-COF and CNT, electrical resistance of the composite membranes was measured using the four-point probe method **(**Fig. 2c**)**. To simplify the optimization process, the total mass of each membrane was fixed to 10 mg. For example, a membrane containing 50 wt% V-COF consisted of 5 mg of V-COF and 5 mg of CNT. Membranes with V-COF contents below 50 wt% exhibited sheet resistance below 1 Ω/sq. However, when the V-COF content exceeded 50 wt%, the resistance rapidly increased by approximately two orders of magnitude. Based on these results, a V-COF:CNT weight ratio of 5:5 was selected for subsequent electrochemical measurements. Further justification for the use of the 5:5 V-COF:CNT membrane is also provided by three-electrode cell measurements discussed in the following section. The BET specific surface areas of the CNT membrane and 5:5 V-COF:CNT membrane were 1103.46 m^2/g and 914.17 m^2/g, respectively **(Figure S10)**. As expected, the micro- to meso-porosity of the V-COF:CNT membrane was lower than that of the pure CNT membrane. However, due to strong π-π interaction between V-COF particles and CNTs, the composite membrane exhibited the formation of larger macropores compared to the dense and compact structure of the pure CNT membrane. These macropores facilitated Nafion electrolyte penetration during hot pressing and improved interfacial adhesion during the actuator device fabrication **(**Fig. 2d, S11**)**.

2.3 Electrochemical and Electromechanical Properties of V-COF:CNT Membranes

To investigate the electrochemical properties of the V-COF:CNT membranes and compare them with pure CNT membranes, cyclic voltammetry (CV) measurements were carried out in a three electrode cell with the V-COF:CNT as the working electrode, a Pt electrode as the counter electrode, and an Ag/AgCl as the reference electrode **(**Fig. 3a**)**. The cell was assembled in a quartz glass cell, which enabled simultaneous displacement measurements of the working electrode using a displacement sensor. The working electrode was prepared by seamlessly adhering the strip of membrane onto a slice of Kapton tape (2 cm x 2 mm). Initially, 1 M LiCl aqueous was used as the electrolyte, but only a small displacement (< 0.5 mm) was observed. This was likely due to the symmetric diffusion of ions, where Li^+ ion diffuse into the electrode under negative bias while Cl^- ions diffuse into the electrode at a comparable rate under positive bias, resulting in a negligible net displacement difference **(**Fig. 3b**)**. To decouple cation and anion diffusion and selectively investigate the electromechanical response associated with Li^+ ion diffusion, 1 M LiTFSI aqueous solution was used as the electrolyte. Bis(trifluoromethanesulfonyl)imide ($TFSI^-$) ions are well known for their bulky and weakly-coordinating nature, leading to diffusion of dissociated hydrated Li^+ ions and high Li^+ ion transport number.[30]

For the CVs, 5:5 and 8:2 V-COF:CNT membranes were cycled within the range of -1.6 V-0.5 V, with an increasing scan rate from 5 mV/s to 200 mV/s. CNT membrane was only cycled within the range of -1 V-0.5 V to avoid water electrolysis. The potential range was also fixed at lower scan rates accordingly to avoid water electrolysis for V-COF:CNT membranes as well. As shown Fig. 3c-e, pure CNT membrane did not exhibit identifiable redox peaks while V-COF:CNT displayed two pairs of pronounced reversible redox couples, which corresponded to the two-step reduction of the bipyridinium moieties, indicative of pseudocapacitive charge storage behavior of the electrode. The first reduction, commenced around − 0.7 V, is assigned to the reduction of viologen dication to the radical cation ($V^{2+} \rightarrow V^{\bullet+}$), and the second reduction, commenced around − 1.3 V, is assigned to the reduction of the radical cation to the neutral state ($V^{\bullet+} \rightarrow V^0$). At a scan rate of 40 mV/s, where the redox peaks are well resolved, the calculated area specific capacitances of the membranes were 42.2, 136.5, 142.2 mF/cm^2 for CNT, 5:5 V-COF:CNT, and 8:2 V-COF:CNT, respectively (**Figure S12)**. Compared to pristine CNT, the specific capacitance of the composite electrodes increased by around threefold, which can be attributed to the pseudocapacitive contribution arising from the redox-active V-COF. Across all scan rates, 8:2 V-COF:CNT membrane exhibited larger peak-to-peak separation between the corresponding oxidation and reduction peaks compared to the 5:5 V-COF:CNT membrane. This increased peak separation indicates sluggish charge-transfer kinetics, resulting from reduced electronic conductivity and hindered ionic transport due to the lower CNT content.

To further analyse the charge storage mechanism, *b*-value analysis was conducted on the 5:5 and 8:2 V-COF:CNT membranes by linearly fitting the plot of logarithm of peak current density versus the logarithm of the scan rate **(**Fig. 3f, S13**)**. The relationship between current (*i*) and scan rate (*v*) follows:[31]

$$i = av^b \qquad (1)$$

$$\log i = \log a + b \log v \qquad (2)$$

where *i* represents the peak current, and *v* stands for the scan rate. A *b*-value closer to 1 indicates a surface-controlled capacitive process, whereas a value near 0.5 indicates diffusion-limited process. All linear regressions showed excellent goodness of fit, with R^2 values greater than 0.99 **(Table S1, S2)**. Although the *b*-values associated with the second reduction peak were identical for both electrodes, the *b*-value for the first reduction peak for 8:2 V-COF:CNT (*b* = 0.634) was closer to 0.5 compared to 5:5 V-COF:CNT (*b* = 0.752). This indicated that the first reduction process in the 5:5 V-COF:CNT was more strongly governed by surface-controlled process, whereas 8:2 V-COF:CNT showed a greater diffusion-controlled contribution, likely due to increased ion transport limitations associated with the higher loading of the V-COF. In contrast, the *b*-values for the anodic peak current densities were higher and closer to 1 for both redox processes, consistent with the surface-controlled process dominated by CNT, as viologen species were partially auto-oxidized by the dissolved oxygen in the electrolyte.[32]

To evaluate the feasibility of the V-COF:CNT electrode for ionic actuator, previously mentioned three electrode setup was used to measure the actuation under Li^+ ion diffusion under negative bias. Two different cathodic potentials were applied (-1 V and − 1.5 V) to trigger each of the reduction reactions, followed by 0.2 V anodic potential. Each potential was applied for 20 s to ensure sufficient time was given to reach its maximum displacement. The anodic potential was maintained at a low value to minimize anion diffusion. The displacement sensor was positioned at the tip of the electrode. When − 1.0 V/0.2 V was applied for the first reduction ($V^{2+} \rightarrow V^{\bullet+}$), both the 5:5 and 8:2 V-COF:CNT electrodes exhibited higher displacement values of 2.00 mm and 1.28 mm, respectively, compared to the CNT electrode (0.71 mm), indicating that the increased capacitance of the pseudocapacitive electrodes translated into larger electromechanical displacement **(**Fig. 3g**)**. However, when the V-COF:CNT ratio was increased to 8:2, the displacement decreased significantly, which is attributed to the reduced contact between the V-COF and the conductive CNT network, resulting in excess V-COF that did not effectively undergo redox reaction. This trend was also observed in the charge and current density responses of the electrodes, where the composite electrodes accumulated nearly twice the charge density during chronoamperometry, arising from the pseudocapacitive nature of the V-COF:CNT electrodes **(Figure S14, S15)**. The same trend was observed when − 1.5 V/0.2 V was applied for the second reduction ($V^{\bullet+} \rightarrow V^0$). 5:5 V-COF:CNT had the highest displacement (2.93 mm), followed by 8:2 V-COF:CNT (1.99 mm) and CNT (1.34 mm) (Fig. 3h, S16, S17**)**. Overall, although increasing the V-COF content enhanced pseudocapacitive charge storage, excessive V-COF loading led to degraded charge-transfer kinetics and reduced actuation performance due to limited electronic contact. The 5:5 V-COF:CNT ratio therefore provided the most effective balance and was identified as the optimal composition for device fabrication.

2.4 V-COF-based ECA

After confirming the actuation performance of the single V-COF:CNT electrode and the composite ratio to 5:5, ECA capable of working in air was assembled by sandwiching two V-COF:CNT electrodes with

$LiBF_4$:$EMIMBF_4$:Nafion membrane. Initially, Nafion membranes incorporating LiTFSI and EMIMTFSI were also investigated to maintain consistency with the experimental results from the three-electrode configuration. However, the bulky and weakly coordinating nature of $TFSI^-$ anions induced phase separation within the Nafion membrane and poor interfacial adhesion between Nafion and V-COF:CNT membranes during hot pressing. This phenomena was likely due to the hot-pressing temperature (130°C) exceeding the ion-relaxation temperature associated with interactions between $TFSI^-$ salts and functional groups in Nafion.[33] Therefore, an $EMIMBF_4$:$LiBF_4$ electrolyte incorporated in Nafion was employed for the ECA, owing to the favorable cation-anion size disparity and the rapid ion migration.[15] CV measurements performed in a three-electrode configuration using the $EMIMBF_4$:$LiBF_4$ electrolyte showed the same characteristic viologen redox peaks, confirming that the redox behavior of V-COF was retained under the electrolyte conditions used for ECA fabrication **(Figure S18)**. A Li^+ ion salt was introduced to provide a mobile counter-ion for charge compensation during viologen reduction, as the electron-transfer process can be limited by the sluggish diffusion and relaxation of bulky ions.[34] The detailed ECA fabrication method can be found in **Supplementary Methods**. The hot-pressed V-COF:CNT || $EMIMBF_4$:$LiBF_4$:Nafion || V-COF:CNT ECA exhibited good interfacial adhesion, with electrode layer thickness of 16–20 μm and electrolyte layer thickness of 70–80 μm as the electrolyte layer, resulting in a total device thickness of 100–120 μm **(**Fig. 4a**)**. The good interfacial adhesion is attributed to the chemical compatibility between the ionic groups of Nafion and the cationic framework of V-COF, together with the increased macropores that facilitates Nafion penetration into the V-COF:CNT membrane during hot-pressing. In contrast, fabrication of an ECA using a CNT membrane with the same Nafion membrane as a control was unsuccessful, owing to insufficient and inconsistent interfacial adhesion between Nafion and the hydrophobic CNT networks. Consequently, characterization was only done for V-COF-based ECA.

The bending behavior of the resulting ECA was characterized using a cantilever beam model, in which the strain was calculated from the bending curvature and the displacement. The V-COF:CNT-based ECA exhibited increasing reversible actuation up to ±2.5 V, where the actuation was caused by the diffusion of $EMIM^+$ and Li^+ ions toward the negatively-biased electrode **(**Fig. 4b, **Supplementary Movie 1, 2)**. It is important to note that, unlike capacitive ECAs based on CNT or PEDOT:PSS, which are typically driven using waveform generators to measure actuation responses, the V-COF:CNT ECA strictly required operation with a potentiostat, with the reference set to the counter electrode. When driven using a waveform generator with the reference effectively fixed at ground, the V-COF:CNT ECA exhibited minimal actuation (< 0.5 mm up to ± 3.0 V), as the V-COF did not undergo effective redox reactions under these conditions. This behavior indicated that the actuation mechanism of the V-COF:CNT ECA was dominated by redox processes of the V-COF, rather than by conventional capacitive electric double-layer charging (EDLC). As expected of the pseudocapacitive electrodes, the CV curves of the symmetric ECA exhibited redox peaks, and the resulting areal specific capacitance (117.01 mF/cm^2) was comparable to that obtained from the three-electrode setup measurements **(Figure S19)**. Compared with the three-electrode configuration, however, the viologen redox peaks were less resolved in the symmetric cell because the

measured voltage represents the total cell voltage distributed across both electrodes and internal resistive/polarization losses, which convolutes the individual electrode redox responses.[35,36] Although, partial dehydration of Nafion caused by the high temperature and pressure during hot-pressing resulted in a relatively high bulk Nafion resistance ($6.34 \cdot 10^{-4}$ S/cm), effective Nafion penetration into the porous V-COF:CNT membrane resulted in a low interfacial charge transfer resistance **(Figure S20)**.

Under square-wave potential of ±0.5, ±1.0, ±1.5, ±2.0, and ±2.5 V at 0.1 Hz, the ECA showed increasing actuation up to maximum peak-to-peak displacement of 0.17, 0.63, 1.87, 2.46 and 5.10 mm, respectively, corresponding to bending strains of 0.09, 0.33, 0.94, 1.18, and 1.86% **(**Fig. 4c,d**)**. During the measurement, the applied potential was limited to ±2.5 V to ensure the stability of both the electrolyte and the V-COF. At higher frequencies, the ECA maintained a fast response under an applied potential of ±1.5 V, showing peak-to-peak displacements of 1.66, 1.55, 1.30, 1.10, 0.66, and 0.42 mm at frequencies of 0.1, 0.2, 0.5, 1, 2, and 5 Hz, respectively, with a response time of 2.8 s **(**Fig. 4e**)**. For blocking force (F_{block}) measurements, because a well-defined equilibrium position was difficult to establish, the ECA was driven between two maximum strain states. The measured peak-to-peak F_{block} was then divided by two to obtain the F_{block}. Under square-wave potential of ±0.5, ±1.0, ±1.5, ±2.0, and ±2.5 V at 0.1 Hz, the ECA showed increasing F_{block} of 0.38, 0.69, 1.01, 1.15, and 1.34 mN respectively **(**Fig. 4f**)**. For comparison with previously reported actuators, the F_{block} was normalized by removing dimensional parameters, yielding normalized F_{block} 0.12, 0.22, 0.32, 0.36, 0.42 MPa, respectively **(**Fig. 4g**)**. This corresponded to load-bearing capacities of 36.8 and 46.9 times of the weight of the entire device at applied potentials of ±1.5 and ±2.5 V, respectively. The device showed excellent cycling stability, with a displacement retention of 129.1% after 10,000 cycles under square-wave potential of ±1.5V at 0.1 Hz. The gradual increasing displacement was likely due to the gradual rehydration of Nafion under ambient conditions (50–60% relative humidity), which enhanced ion penetration into the electrode **(**Fig. 4h**)**. Although extended cycling was performed, the ECA began to show decay past 10,000 cycles. Rehydration effects were also observed during device aging. Cyclic voltammetry performed after exposure of the device to ambient conditions for two months showed increased current density and a more distinct redox peak, indicating that the V-COF remains stable under ambient conditions and that water content plays a critical role in device performance **(Figure S21)**. Overall, the combination of large bending strain, fast response, high blocking force, and long-term cycling stability places the V-COF-based ECA among competitive recently reported electrochemical actuators **(Table S3)**.

Interestingly, unlike capacitive ionic actuators, which typically show a linear displacement-voltage response at low potentials, following the capacitance-charge-voltage relationship, and a plateau at higher voltages due to ion saturation, the V-COF-based actuators exhibited a stepwise actuation process governed by the redox-states of viologen. Two distinct jumps in bending strain was observed at ±1.5 V and ±2.5 V, which corresponded to the first ($V^{2+} \rightarrow V^{\bullet+}$) and second ($V^{\bullet+} \rightarrow V^{0}$) reduction reactions. A similar redox-state-dependent increase was observed in F_{block}, although the transitions were less sharply resolved than in the free-displacement response. This behavior is consistent with the constrained nature of blocking-force measurements, where redox-induced strain is converted into stress and becomes

additionally influenced by actuator stiffness, viscoelastic relaxation, and probe-contact stress transfer.[37,38] Therefore, the force response may be mechanically broadened, even when the displacement response clearly followed the discrete viologen redox transitions. Overall, this two-step redox-switchable behavior enables discretized, state-dependent mechanical outputs that are difficult to access in conventional capacitive actuators, allowing voltage-programmed control over both actuation amplitude and force. Such multistate actuation is particularly attractive for applications requiring controllable mechanical states rather than simple continuous motion, including adaptive mechanical interfaces and electrically programmable actuators.

2.4 Actuation Mechanism of V-COF-based Electrode.

Various in-situ and ex-situ characterizations were performed to investigate the actuation mechanisms in the V-COF-based electrodes. Firstly, ex-situ electrochemical X-ray absorption near-edge structure (XANES) was used to elucidate the atomic structure of the V-COF under applied cathodic potential from 0 V to -1.2 V. The N K-edge XANES spectra exhibited a distinct resonance at 400.6 eV, the resonance lied closer to the energy region commonly associated with graphitic-type N in conjugated carbon systems than pyridinic-type N **(**Fig. 5a**)**.[39,40,41,42] This result indicated strong electronic coupling within the conjugated V-COF framework, which helped stabilize the viologen-based redox states during electrochemical cycling. Upon applying potentials of -0.4 to -0.6 V, the resonance was shifted to 401.2 eV, indicating a change in the local nitrogen electronic structure associated with one-electron reduction of viologen dication (V^{2+}) to radical cation ($V^{\bullet+}$). The shift suggested that the electron density introduced upon radical-cation formation was partially delocalized across the conjugated V-COF backbone, with solvent and counterion interactions likely introducing partial local electronic asymmetry.[43,44,45] Upon further reduction to the neutral state (V^0) at more negative potentials, the resonance returned to 400.8 eV, indicating a further reorganization to a symmetric N electronic structure upon second electron transfer.[46] Reoxidation back to the dication state yielded similar spectra as the initial, supporting the reversibility of the V-COF redox processes. As the prepared electrode was 5:5 V-COF:CNT, the C K-edge spectra were dominated by the π* C = C (285.5 eV) and σ* C–C (~ 292 eV) transitions from the CNT **(**Fig. 5b**)**.[39,47] To extract redox-dependent contributions from the V-COF component, integrated peak-area ratios were compared for the π^*C–N/C = N resonance near 286.8 eV and the low-energy defect-/π-derived resonance near 284.1 eV, each normalized to the dominant π^*C = C feature **(**Fig. 5d**)**. Both ratios increased in the radical-cation state, suggesting that viologen radical formation modified the local π-electronic structure of the V-COF/CNT composite.[48,39] These changes were consistent with transient radical-induced electronic asymmetry and enhanced structural/electronic adaptability of the conjugated framework during electrochemical actuation.

For in-situ Raman spectroscopy, a separate electrode was prepared by casting V-COF:Nafion composite on indium tin oxide (ITO) substrate to avoid the strong Raman signals from CNT **(Figure S22)**.[49,50] The in-situ spectra exhibited four distinct regions: S = O related vibrations from the $TFSI^-$ anion (960–1100 cm^{-1}, red), pyridinium N-associated vibrations (1225 cm^{-1}, yellow), disorder- or radical-sensitive bands (1380

cm^{-1} and 1515 cm^{-1}, green and blue), C = C aromatic stretching (1604 cm^{-1}, grey), and C = N imine stretching (1640 cm^{-1}, grey) **(**Fig. 5e**)**.[26,51] Under cathodic bias, the $TFSI^-$-related bands showed negligible intensity changes, suggesting that the local $TFSI^-$ environment was not strongly perturbed during reduction. The sharp pyridinium N peak at 1225 cm^{-1} was shifted to a peak with lower intensity at 1237 cm^{-1}, indicating the reduction of pyridinium and the coordination with Li^+ counterions. The disorder-/radical-sensitive bands reached maximum intensity near − 0.5 V, supporting transient radical-induced electronic asymmetry and local structural reorganization within the conjugated framework. Upon reoxidation to the dication state, the pyridinium/viologen-associated band recovered, supporting the reversibility of the V-COF redox process. Overall, the in-situ Raman spectra indicated that V-COF actuation was governed by reversible viologen redox chemistry coupled with ion-compensated structural and electronic reorganization.

Finally, to assess whether the reduction-induced expansion of V-COF was a key contributor to actuation, in-situ XRD measurements were conducted in reflection mode using a symmetric cell configuration that mimicked the ECA device structure (V-COF:CNT || $LiBF_4$:$EMIMBF_4$@Celgard2500 || V-COF:CNT) (**Figure S23)**. Stepwise potentials were applied during the measurement, alternating between 0.5 V for the oxidized state (V^{2+}) and − 1.5, − 2.0, or − 2.5 V for the reduced state (Fig. 5c**)**. Compared to the (200) diffraction angle in the oxidized states (~ 4.14° at 0.5 V), the diffraction peaks of the reduced states ($V^{\bullet+}$, V^0) shifted to a lower diffraction angle (~ 4.09° at -2.5 V), which corresponded to approximately 1.22% strain in the $d_{(200)}$ direction. Electron injection into the viologen-containing framework during reduction likely redistributed charge density and modified bond order within the conjugated network, leading to framework elongation.[46] To evaluate the feasibility of redox-induced strain in the V-COF lattice, DFT calculations were performed on a representative lattice segment containing a central viologen moiety **(**Fig. 5f**)**. As each of the four connecting arms required a complete viologen unit, the model comprised a total of five viologen units to represent a lattice segment of V-COF. To assess the lateral dimensional change across the central viologen unit, the distance between the two imine nitrogen atoms located on opposite sides of the viologen moiety was compared among the three redox states (V^{2+}, $V^{\bullet+}$, V^0). The distance increased progressively with sequential reduction, from 18.319 Å for V^{2+} to 18.332 Å for $V^{\bullet+}$ and 18.393 Å for V^0, corresponding to an overall linear strain of approximately 0.4%. The calculated strain was smaller than the experimentally observed strain, which may be attributed to structural relaxation in the isolated model through rotation of the terminal linkers and out-of-plane distortion. Such relaxation is expected to be more restricted within the extended V-COF lattice, potentially resulting in a larger in-plane strain. Together with ion redistribution and EDLC formation at the V-COF/electrolyte interface, this reversible redox-induced lattice expansion contributed to the high actuation strain and blocking force of the V-COF-based ECA. Moreover, the retention of the peak shift over successive in-situ XRD cycles further supported the reversibility of the redox-induced structural expansion.

The combined in-situ and ex-situ spectroelectrochemical measurements revealed that V-COF actuation originated from reversible viologen redox chemistry coupled with ion-compensated charge transport and

redox-induced framework expansion. These coupled electronic, ionic, and structural changes collectively governed the efficient electromechanical response of the V-COF-based ECA. Compared with conventional one-dimensional polymer actuators, the two-dimensional COF architecture provided an ordered layered framework that enabled more directional redox-induced expansion, allowing molecular-level structural changes to be more effectively translated into macroscopic actuation.

2.5 Applications of V-COF-based ECA

Following confirmation of the redox-driven structural evolution and actuation mechanism, the applicability of V-COF as the primary active material in electrochemical actuators was evaluated using two representative device demonstrations: a two-claw gripper and a two-legged crawler. Owing to the stepwise increase in blocking force arising from the redox-driven actuation mechanism, the grasping strength of the gripper could be modulated between weak gripping at ±1.5 V and strong gripping at ±2.5 V, enabling voltage-dependent force control. Under weak gripping, associated with the first reduction reaction from V^{2+} to $V^{\bullet+}$, the gripper lifted a light object with a mass 1.85 times that of the electrodes **(**Fig. 6a, **Supplementary Movie 3)**. Under strong gripping, associated with further reduction toward V^{0}, the gripper lifted a heavier object with a mass 6.58 times that of the electrodes **(**Fig. 6b, **Supplementary Movie 4)**. The two-legged crawler was fabricated by attaching PET-reinforced copper-tape legs to the V-COF-based ECA, creating a frictional bias that enabled two-anchor crawling motion **(**Fig. 6c, **Supplementary Movie 5)**. Owing to the high blocking force of the actuator, the crawler travelled 3 cm within 70 s under an applied voltage of ± 2.0 V, showing locomotion performance comparable to recently reported soft crawlers with similar form factors **(Table S4)**. This result indicated that the V-COF-based ECA generated sufficient force to overcome static friction against the paper substrate while transporting the PET-supported body. Overall, these demonstrations confirm that the redox-state-dependent force output of the V-COF-based ECA can be translated into practical device functions, including voltage-programmed gripping and locomotion. The ability to access distinct mechanical states through redox switching provides a route toward soft robotic components that can adapt their output force and movement according to the applied electrical stimulus.

3. Discussion

In conclusion, this work establishes a viologen-based cationic COF as a primary redox-active framework for low-voltage electrochemical actuation. The ordered charged framework integrates accessible ion-transport pathways with reversible bipyridinium redox centers, enabling ion-coupled electron transfer to drive lattice expansion and macroscopic bending. When combined with CNTs, the optimized V-COF:CNT electrode achieved an effective balance between charge storage, electronic conductivity, and ion accessibility, yielding a peak-to-peak bending strain of 1.86%, a response time of 2.8 s, high blocking force, and stable operation over 10,000 cycles. Various in-situ and ex-situ spectroelectrochemical analyses further confirmed that the actuation arises from reversible viologen redox switching coupled with Li^{+} counterion migration and framework expansion. The discrete redox transitions produced stepwise mechanical outputs and provide the first example of a V-COF-based ECA showing redox-state-

dependent force output, enabling voltage-programmed gripping and actuator-driven crawling. By coupling redox reactions within an ordered 2D framework to controllable macroscopic motion, this study highlights redox-active ionic COFs as a promising platform for durable electromechanical materials and soft robotic systems requiring tuneable force output under low electrical bias.

Declarations

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Contributions

JUC conceived the project, designed and performed the experiments, analyzed the data, and wrote the manuscript. YZ contributed to the conceptual development and experimental design. JS, YHQ, BR, AG, JL assisted with data collection and data analysis. PSL provided project supervision, contributed to the project design, and secured funding. All authors reviewed and approved the final manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability

The data that support the findings of this study are available in the Source Data file. Source data are provided with this paper. All data are available from the corresponding author upon request.

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