Interaction of Polar and Nonpolar Polyfluorenes with Layers of Two-Dimensional Titanium Carbide (MXene): Intercalation and Pseudocapacitance

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ABSTRACT: This article provides insight into the interaction of synthetic conjugated polymers [polyfluorene derivatives (PFDs)] with layers of two-dimensional titanium carbide (Ti$_3$C$_2$T$_x$). Three derivatives with nonpolar, polar, and charged nitrogen-containing functionalities were synthesized via the Suzuki polycondensation reaction. The organic–inorganic PFD/Ti$_3$C$_2$T$_x$ hybrids were prepared and characterized using X-ray diffraction and a range of microscopic and spectroscopic techniques to elucidate the host–guest interaction mechanism. We show that polar polymers with charged nitrogen-containing ends have the strongest interaction with the Ti$_3$C$_2$T$_x$ layers, yielding an increase in interlayer spacing and large shifts in spectroscopic peaks. Furthermore, the effect of polymer backbone juxtaposition between Ti$_3$C$_2$T$_x$ layers on pseudocapacitance is discussed in detail. Our results suggest that new organic materials capable of intercalation between the layers of Ti$_3$C$_2$T$_x$ and other MXenes may be used in the design of hybrid structures for high-performance energy storage applications and beyond.

Two-dimensional (2D) materials have garnered immense interest, particularly since the discovery of the unique physical properties of graphene. A large family of 2D transition metal carbides and nitrides (MXenes), which offers attractive structural diversity, metallic conductivity, and hydrophilicity, was reported in 2011. The MXenes are synthesized by selectively etching the A element layers from ternary transition metal carbides and/or nitrides with a general formula of M$_{n+1}$AX$_n$ (M = an early transition metal, e.g., Ti, V, Mo, etc.; A = group XIII and XIV element; X = C/N; and n = 1, 2, or 3). After wet chemical etching, surface functional groups (T$^x$) such as F, O, and OH terminate the MXene surface. As a result, the MXene compositions are generally represented as M$_{n+1}$X$_n$T$^x$. Despite its short history, the MXene family has already shown great potential in various applications such as supercapacitors, batteries, water purification, catalysis, antibacterial films, transparent conductive electrodes, and others. Intercalation of metal ions and organic molecules and incorporation of carbon particles and polymers between MXene layers can be used to control and modify the properties of MXenes. For instance, Lukatskaya et al. intercalated various metal cations between Ti$_3$C$_2$T$_x$ MXene, which led to a high volumetric capacitance. The incorporation of carbon nanoparticles between MXene layers helped to prevent their compact stacking and further enhanced their capacitive performance. Mashtalir et al. intercalated various organic molecules (urea, hydrazine, DMF, DMSO, etc.) between Ti$_3$C$_2$T$_x$ layers, allowing their delamination into nanometer-thick flakes, leading to significantly improved performance in Li-ion batteries and, more recently, in supercapacitors. On the basis of a similar concept, Naguib et al. recently intercalated various large organic bases [tetraethylammonium hydroxide (TBAOH)], choline hydroxide, or n-butylamine to delaminate V$_2$CT$_x$ and Ti$_3$CNT$_x$ MXenes. Halim et al. and Mashtalir et al. used TBAOH and isopropanol to produce single-layer Mo$_2$CT$_x$ and Nb$_2$CT$_x$ MXene flakes, respectively, both of which showed improved electrochemical performance compared to that of their multilayer counterparts. Nanoscale design of materials, such as the incorporation of polymers into MXene layers, is a promising route for further expanding the applications of MXenes by manufacturing functional hybrid materials with useful chemical, physical, mechanical, and electrochemical properties. 2D materials like graphene and MoS$_2$ aggregate through van der Waals...
interactions in polymer matrices. Unlike graphene, MXenes offer high conductivity in combination with reactive surface chemistry and hydrophilicity, which may provide a unique platform for the synthesis of MXene/polymer hybrids with controlled morphology, thickness, conductivity, and mechanical strength. Recently, Zheng et al. intercalated poly(vinyl alcohol) (PVA) between MXene flakes and obtained PVA/MXene hybrid films with high electrical conductivity, good mechanical strength, and superior supercapacitor performance. Capacitance was further improved when polypyrrole (PPy) chains were confined between MXene layers because of the redox behavior of PPy. Naguib et al. synthesized conductive MXene/polyacrylamide hybrids with high polymer loadings. To further improve the properties of the material, it is necessary to gain a fundamental understanding of the interaction of polymers with MXene surfaces.

The idea of using conjugated polymers (CPs) as electrochemically active materials with MXenes is very intriguing. The former provides a unique set of properties, including a variable band gap, controlled exciton and charge transport, processability, and water solubility, and the latter provides a conductive and mechanically strong support. The use of preformed CPs with defined chemical and physical characteristics could provide new insight into interaction mechanisms, which subsequently could be used to tune the physical, chemical, and electrochemical properties of the resulting CP/MXene hybrids. The evolution toward improved polymeric materials moved us to substituted poly(9,9-dioctylfluorene) (PFO). Among the broad class of CPs, PFO plays an important role because of its wide range of desirable properties, such as high charge-carrier mobility, good thermal stability, and good solution processability together with the ability to tune the end group chemistry. The ability to synthesize PFO with controlled end functionalities allows us to control the strength of the interaction of MXene with polymers and manufacture MXene/polymer hybrids with favorable physicochemical and electrochemical properties.

Herein, we synthesized a family of PFOs having the same conjugated backbone but different lateral chains, namely, apolar, polar, and end-charged group alkyl chains, to investigate the interaction mechanism that leads to separation of Ti3C2Tx layers. PFOs with no polar functionality (P1), a polar nitrogen (P2), and charged nitrogen groups (P3) were synthesized via the Suzuki polycondensation reaction between dibrominated fluorene and a bis-borolane fluorene derivative. We chose Ti3C2Tx MXene as a model system because it is the most studied and well understood MXene. We further discuss the impact of the interaction of the polymer with Ti3C2Tx layers on the pseudocapacitance of the organic/inorganic hybrid electrodes.

Figure 1 provides a general overview of our approach to studying mechanisms of interaction of Ti3C2Tx layers with PFDs having the same p-conjugated backbone but different lateral alkyl chains (Figure 1), where P1 stands for poly(9,9-dioctylfluorene), P2 for poly(9,9′-bis[3-(N,N-dimethylamino)propyl]-2,7-fluorene-alt-2,7-(9,9-di hexylfluorene)), and P3 for poly(2,7-(9,9′-dicetyl)fluorene-alt-2,7-[9,9′-bis(5′-trimethylammonium bromide)hexyl]fluorene). While P1 is completely nonpolar, the polarity on P2 stems from the nitrogen-containing groups on the dimethylamino side chains, and P3 is further functionalized with trimethylammonium ionic groups stabilized with Br− counterions. These systems were further substituted with octyl side chains to deter intermolecular aggregation.

Another purpose of functionalization with trimethylammonium ionic groups was to make the P3 polymer somewhat resemble TBAOH, which can intercalate between MXene layers. As a result, on the basis of our understanding of interaction and/or intercalation of P3, we may also be able to shed light on TBAOH/MXene interactions that were used to improve the electrochemical performance of MXene. To explore polymer/MXene interaction mechanisms, we prepared hybrids by mixing together the polymer and Ti3C2Tx at 1:2 weight ratios at room temperature. Free-standing films of P1@Ti3C2Tx, P2@Ti3C2Tx, and P3@Ti3C2Tx were prepared by vacuum filtration followed by vacuum drying up to 48 h. Because of the loss during filtration and washing, the resulting polymer contents of these films were approximately 2, 5, and 10 wt %, respectively. The mass loading of polymers on the MXene was determined by weighing the vacuum-dried MXene-based films before and after the incorporation of the polymer using an ultramicro balance (Mettler Toledo UMX2, repeatability of 0.9 µg) with a high accuracy of up to 1 µg. Different contents of the polymer after filtration suggested different strengths of their interaction with MXene flakes. During mixing, only 2 wt % P1 polymer was preserved, which indicated that it showed the weakest interaction with the MXene surface. This can be ascribed to the noninteracting end groups of P1, and most of the polymer was filtered out during the washing process. On the other hand, the P3 polymer showed the strongest interaction with the MXene surface. To support further the greater extent of P3 intercalation compared to that of P2, which is mostly adsorbed on the surface, we performed fluorescence microscopy on P2 and P3 polymer hybrids. The obtained top view micrographs evidenced the presence of segregated fluorescent clusters (P2) on a black background (MXene) in P2@Ti3C2Tx, while in P3@Ti3C2Tx, the fluorescent emission was diffused more uniformly on the whole surface (Figure S1). Further synthesis details of polymers and hybrids are provided in the Experimental section of the Supporting Information.

The cross-sectional scanning electron microscopy (SEM) image of P3@Ti3C2Tx (Figure 2a) shows well-aligned Ti3C2Tx layers in the hybrid film. Similar cross-section morphologies were observed for the P1@Ti3C2Tx and P2@Ti3C2Tx films. Compared with the X-ray diffraction (XRD) pattern of pristine
Ti$_3$C$_2$Tx films (Figure 2b), that of P1@Ti$_3$C$_2$Tx exhibited a slight shift and that of P2@Ti$_3$C$_2$Tx showed a noticeable shift (probably due to nitrogen-containing ends) in the c-lattice parameter (c-LP). On the other hand, P3@Ti$_3$C$_2$Tx showed a much larger downshift toward from 7.23° for Ti$_3$C$_2$Tx to 5.34°. This shift corresponds to an expansion in c-LP from $\approx$24.47 Å for Ti$_3$C$_2$Tx to $\approx$33.01 Å, which may be attributed to juxtaposition of the P3 macromolecules between Ti$_3$C$_2$Tx layers via charged ends. The shift in c-LP is associated with the remaining amount of polymers between the MXene layers after washing and translates into interaction of the polymer with the MXene. Our systematic investigation shows that the trend of the increase in the lattice parameter follows the polarity of the side chains of the polymers, indicating that the interaction strength drives the reticular expansion. This is because the stronger the interaction between polymers and MXenes, the more the polymer will be retained between MXene flakes after the filtration, leading to larger c-LP. In this case, charged polymers exhibited the strongest interaction [Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS)]; thus, a large amount of the P3 polymer remained between MXene layers, leading to a large c-LP, while very little nonpolar polymer was incorporated. XRD patterns of Ti$_3$C$_2$Tx, P1@Ti$_3$C$_2$Tx, P2@Ti$_3$C$_2$Tx, and P3@Ti$_3$C$_2$Tx films are reported for larger angles in Figure S2, indicating that the main structural features are recurring; however, a detailed study aiming to pinpoint fine differences that can be attributed to new phases developed will be reported in the future.

The presence of the P3 polymer between the Ti$_3$C$_2$Tx flakes is further confirmed by the cross-sectional transmission electron micrographs (Figure 2c,d). It is obvious from Figure 2d that polymer chains (bright layers) are aligned and confined between Ti$_3$C$_2$Tx layers (dark layers). It is reasonable to believe that the self-assembly starts in the solution because of positively charged lateral chain functionalities of P3, which electrostatically attaches to MXene.

To gain further insights into fundamental chemical and physical interactions that dictate the formation of the MXene/polymer architecture, it is necessary to probe the functionalities that induce peculiar interactions with polymers. We attempted to accomplish this task by using various spectroscopic tools. We performed FTIR on all the samples (Figure 3a−d).

The FTIR spectra of P1 and P1@Ti$_3$C$_2$Tx films (Figure 3a) show no obvious changes in the P1@Ti$_3$C$_2$Tx spectrum, which

![Figure 2.](image)

**Figure 2.** (a) Low-magnification SEM image of a P3@Ti$_3$C$_2$Tx film. (b) XRD patterns of the hybrids and pure Ti$_3$C$_2$Tx. The c-LP for each hybrid is given above the corresponding XRD pattern. (c) TEM micrograph of a few layers of pristine Ti$_3$C$_2$Tx. (d) TEM image of aligned P3 chains (bright layers) between Ti$_3$C$_2$Tx (dark layers).

![Figure 3.](image)

**Figure 3.** FTIR spectra of the polymers and hybrid films. (a) P1, polymer bearing a nonpolar end (bottom, black line) and P1@Ti$_3$C$_2$Tx (top, red line). (b) P2, polymer with a polar nitrogen (bottom, black line) and P2@Ti$_3$C$_2$Tx (top, red line). (c) P3, polymer with a polar charged nitrogen end (bottom, black line) and P3@Ti$_3$C$_2$Tx (top, red line). (d) Close-up of the fingerprint region of panel c (green area) to show the peak shifts due to interaction of P3 charged ends with the Ti$_3$C$_2$Tx surface.
is most likely caused by the lower polymer content and weakest interaction of P1 with MXene. The absence of dimethyl sulfoxide (DMSO) in the P1@Ti3C2T_x hybrid film is evident because of diminished DMSO peaks (Figure S3). Moreover, the FTIR spectrum of the pristine Ti3C2T_x film shown in Figure S3 appeared to be featureless. The peaks in Figure 3a are assigned as 812 (ν, CH), 1266, 1260 (ν, CN), 1375 (ν_m (CH)), 1450 (ν, CH2), 2853 (ν, CH3), 2926 (ν, CH2), and 3023 and 3060 (ν, CH, aromatic).30−33 P2@Ti3C2T_x showed some interaction, deduced from the appearance of the weak peaks associated with P2 and the presence of the CN vibrations at 1166 and 1260 cm−1 (Figure 3b).34 The peaks in Figure 3b are assigned as 812 (ν, CH), 1166, 1260 (ν, CN), 1375 (ν_m (CH)), 1450 (ν, CH2), 2853 (ν, CH3), 2926 (ν, CH2), and 3023 (ν, CH3).30−33

In sharp contrast to those of P1 and P2, FTIR spectra of the P3@Ti3C2T_x film (Figure 3c) exhibited the most polymer peaks, which confirmed the presence of a large amount of the P3 polymer in the sample (~10 wt %). The plausible factor for the presence of larger amounts of the P3 polymer seems to be the charged quaternary ammonium end group of the P3 polymer. Interestingly, when we magnified Figure 3c from 1150 to 1550 cm−1 (green dashed lines in Figure 3c), we observed strong blue shifts in the P3@Ti3C2T_x spectrum. Most importantly, the largest shifts were associated with the cationic ends of the P3 polymer (Figure 3d). Qualitatively, this suggests that the cationic end of the P3 polymer plays a crucial role in interaction with the Ti3C2T_x surface. The peaks in panels c and d of Figure 3 are assigned as 30−32,34,35 812 (ν, CH), 965 (ρ, CH2), 1257 (ν, CN), 1377 (δ, RCH3), 1402 (δ, CH2N+), 1415 (ν, HN+), 1457 (ν, CH), 1480 (δ, CH3N+), 2853 (ν, CH3), 2926 (ν, CH2), and 3007 and 3060 (ν, CH).

Two plausible interactions are possible at the organic–inorganic interface: (1) electrostatic interactions, because of the presence of a charged nitrogen-containing group (CH3−N+), and (2) hydrogen bonding with the surface functional groups (O or F) of Ti3C2T_x. Because P3 has bulky methyl end groups, they act as a spacer and keep the cationic nitrogen center away from the surface functional groups of Ti3C2T_x; thus, hydrogen bonding is less likely to be the dominant interaction.36 On the other hand, the hindrance of hydrogen bond formation promotes the flexible orientation of the cationic end groups at the Ti3C2T_x surface with higher lateral mobility and higher diffusion rates between the MXene layers.36,37 This qualitative description can be extended to explain delamination of various MXenes using TBAOH or other organic bases,16−18 where a charged nitrogen-containing group is surrounded by large C6H4 groups, leading to higher mobility, greater spacing between MXene layers (Figure 2b), and delamination of MXene.

Raman spectroscopy was further used to elaborate the PFO/MXene interactions. Raman spectra for all samples were recorded in the wavenumber range from 150 to 3000 cm−1. We did not observe any peaks beyond 1800 cm−1; therefore, we set it as a cutoff Raman shift (Figure 4a−c). The Raman spectra of Ti3C2T_x, P1, and P1@Ti3C2T_x are shown in Figure 4a. Both P1 and Ti3C2T_x exhibited their typical bands.2 A sharp peak in the P1 spectrum is associated with phenyl ring vibrations of P1.38 It is obvious that the P1@Ti3C2T_x spectrum is dominated by Ti3C2T_x with a negligible signature of P1. This confirms that most of the polymer was filtered out during washing because of weak or no interaction with MXene. In a similar way, when the P2@Ti3C2T_x film spectrum was analyzed, in addition to the Ti3C2T_x peaks, weak P2 peaks were observed, confirming a weak interaction between P2 and the Ti3C2T_x surface. Unlike P1@Ti3C2T_x and P2@Ti3C2T_x spectra, the P3@Ti3C2T_x spectrum exhibited strong signatures of both P3 and Ti3C2T_x, which indicates the presence of a large amount of P3 between the layers or on the surface. All peaks of P3@Ti3C2T_x further confirmed that charged ends in a polymer matrix are crucial for the charge transfer interactions.
broadened and shifted, confirming P3 polymer interaction via the charged ends and confinement between the MXene layers, consistent with previous studies of polyamide, polyaniline, and other polymer/clay hybrids.39−41 Thus, both FTIR and Raman spectra corroborated that the charged nitrogen-containing functionalities may be responsible for the interaction of polymers with Ti$_3$C$_2$T$_x$.

XPS analysis was performed to evaluate changes in the surface chemistry of P3@Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$. Figure 4d shows a shift to a lower binding energy (BE) of the nitrogen species in P3 after intercalation (P3@Ti$_3$C$_2$T$_x$), indicating a shift to a lower oxidation state of the N species. The shift in the N 1s peak to lower BE is due to the bonding of the nitrogen species to an electron donor (MXene). A similar BE shift in the N 1s peak to lower BE is due to the bonding of the nitrogen species as well as the reduction of the Li species; this is like other work where it was shown that the Li species intercalated in Ti$_3$C$_2$T$_x$ was replaced with a K or Rb species upon immersion in their chloride solutions, and we suggest that a similar process is occurring here where Li is being replaced by the P3 polymer where the polymer is interacting with the MXene flakes. The suggested mechanism is based on the change in the BE of the N 1s species as well as the reduction of the Li species; this is like other work where it was shown that the Li species intercalated in Ti$_3$C$_2$T$_x$ was replaced with a K or Rb species upon immersion in their chloride solutions, and we suggest that a similar process is occurring here where Li is being replaced by the P3 polymer where the polymer is interacting with the MXene via the nitrogen species. We further think that LiBr formation takes place, as confirmed by XPS data that show a decrease in Li content and a corresponding increase in N percentage.

As known earlier, we found O, F, and OH terminations, in addition to adsorbed water.44 Because hydrogen bonding is prohibited by the bulky methyl groups of P3, the dominant processes appear to be electrostatic and ion exchange. It is obvious from the formula that all the surface terminations remain the same, except for the −F that has been reduced slightly, while the Li-ion content has been reduced from 0.2 to 0.07 mol/mol of Ti$_3$C$_2$T$_x$. After interaction with P3, the sum of Li ions and N moles is equal to the number of moles of Li ions in Ti$_3$C$_2$T$_x$, suggesting that the polymer replaced Li⁺ between MXene layers. It has been shown that cation exchange can take place in MXenes. For instance, Ren et al.44 showed that treating Li-Ti$_3$C$_2$T$_x$ with CuSO$_4$ resulted in replacement of the Li with Cu ions, which catalyzed the oxidation of MXenes. Similarly, Ghidiu et al. fully exchanged Li ions with K, Na, Rb, Mg, and Ca ions.47 Thus, after the ions had been mixed with P3 in solution, the amount of Li ions is reduced, and they are replaced with charged N-containing polymer ends; this is where the polymer attaches to the MXene flakes. The suggested mechanism is based on the change in the BE of the N 1s species as well as the reduction of the Li species; this is like other work where it was shown that the Li species intercalated in Ti$_3$C$_2$T$_x$ was replaced with a K or Rb species upon immersion in their chloride solutions, and we suggest that a similar process is occurring here where Li is being replaced by the P3 polymer where the polymer is interacting with the MXene via the nitrogen species. We further think that LiBr formation takes place, as confirmed by XPS data that show a decrease in Li content and a corresponding increase in N percentage.

We have shown previously that intercalation of the organic materials and metal cations as well as insertion of carbon nanoparticles between MXene layers leads to an increase in
capacitance due to improved ion accessibility.\textsuperscript{5,13,21,22} In this work, we have observed an increase in interlayer spacing as well as strong interaction of P3 with Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}. This encouraged us to further explore as-synthesized free-standing P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} “paper” as a supercapacitor electrode. The cyclic voltammetry (CV) curves of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} films (Figure 5a) tested in 1 M H\textsubscript{2}SO\textsubscript{4} exhibited pseudorectangular CVs at scan rates between 2 and 100 mV/s. The deviation of CV curves from the rectangular shape, typical for double-layer charge storage,\textsuperscript{4,32} indicates pseudocapacitive behavior of the hybrid film due to a change in Ti oxidation state.\textsuperscript{30,35} It is worth mentioning that the voltage window of the MXene electrodes can usually be extended further to lower negative potentials;\textsuperscript{5,13,21} however, the CVs of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid showed hydrogen evolution below $-0.2$ V. This again suggests an interaction with a possible charge transfer between P3 and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}. Galvanostatic charge/discharge (GCD) at various current densities (5, 10, 12, 15, and 20 A/g) exhibited nearly triangular plots (Figure 5b), which show high reversibility and excellent Coulombic efficiency ($\approx100\%$), after P3 juxtaposition.

To further examine the interaction-dependent charge storage performance, CV curves of P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} were compared with those of pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, P1@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and P2@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid films at 20 mV/s (Figure 5c). The P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes exhibited expanded CVs compared to those of pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, P1-, and P2-based hybrid films. The shape of the CVs of P1 and P2 was like that of pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, but the capacitance values are somewhat lower. The area under the curve for P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} is significantly larger than those of other films, indicating a higher capacitance, which most likely originates from the charge transfer interactions of P3 with the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} layers or a larger opening between MXene layers due to PVA intercalation. Compared to that of the pristine MXene electrodes, the improved capacitance was attributed to the expansion of MXene layers that allows easier access of protons to MXene surfaces (Figure 2). In addition, fluorescence micrographs (Figure S1) show that P2 is segregated while P3 is uniformly mixed with the MXene, further explaining the high capacitance of the P3 polymer-containing hybrid electrodes.

The performance of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes at scan rates between 2 and 100 mV/s is shown in Figure 5d and compared with the literature data. The gravimetric capacitance of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes exceeds 380 F/g at 2 mV/s, which corresponds to a volumetric capacitance of 1026 F/cm$^3$(d $=2.70$ g/cm$^3$), which is close to that of MXene/PPy electrodes,\textsuperscript{22} one of the highest values for any pseudocapacitive material. The gravimetric capacitance is more than twice that of the PVA/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid and more than 1.5 times the highest reported capacitance of the pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} film (245 F/g at 2 mV/s).\textsuperscript{5,32} The highest gravimetric capacitance of P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} was lower (mostly at low scan rates) than that of the PPY/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes due to larger pseudocapacitive contributions from PPY.\textsuperscript{22} However, when the scan rate was increased from 5 to 100 mV/s, PPY and P3 hybrids exhibited similar capacitance values. The large capacitance loss for PPY/MXene hybrid electrodes was attributed to PPY’s inherent challenge of the doping–undoping process during the redox process.\textsuperscript{22} It is known that the presence of quaternary-N offers pseudocapacitive character and assists in charge percolation to improve the electrochemical performance.\textsuperscript{5,32,35} Because P3 contains quaternary-N on side chains, thus enhanced capacitance stems from the pseudocapacitive contributions of the quaternary-N redox reactions and better charge transfer kinetics at the organic/inorganic hybrid interface,\textsuperscript{5,32,35} which led to overall improved electrochemical performance of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid electrodes. Thus, the excellent electrochemical performance of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid is due to the synergistic impact of P3 intercalation, and therefore better proton accessibility, and pseudocapacitive contributions of the P3 polymer. Furthermore, the pseudocapacitance character of the P3 polymer is apparent when compared with those of previously reported PVA/MXene hybrid electrodes in which the same polymer electrolyte content (10 wt %) improved capacitance by only $55$ F/g compared to that of its pristine MXene counterpart.\textsuperscript{21} While PVA is poorly conducting and shows no redox activity, the improved capacitance was attributed to the expansion of layers due to PVA intercalation. Compared to that of the PVA/MXene hybrid, the improvement in the capacitance of the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} hybrid is more significant (Figure 5d), which again confirms a pseudocapacitive contribution of the P3 polymer, similar to the case for PPY/MXene electrodes.\textsuperscript{22}

The polymer-induced changes in the electrical resistance and diffusion limitations of the electrodes were investigated by impedance spectroscopy (Figure 5e). The Nyquist plot of the pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes exhibited a negligible semicircle (Figure S5a) and low charge transfer resistance ($R_a$). Although the hybrid film showed no semicircle and a lower $R_a$ value in the high-frequency region, it displayed a slope in the low-frequency region of the Nyquist plot, best known as the Warburg region, lower than that of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes.\textsuperscript{54} This is indicative of a slower diffusion of protons in the P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} film, presumably because of the presence of the P3 molecules between the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} layers, and may explain the capacitance decay of polymer-containing films at higher scan rates.

A typical problem with polymer-based electrodes is their poor cyclic ability and a limited lifetime.\textsuperscript{55} We performed cycle life tests at scan rates of 20 and 100 mV/s. We first cycled our electrode at 20 mV/s up to 3000 cycles and did not observe any change in capacitance (Figure 5f, inset). Another film was then tested at a higher scan rate of 100 mV/s up to 10000 cycles, and a stable performance was observed at this scan rate, as well (Figure 5f). The identical CVs (Figure S5b) at the 1000th and 10000th cycles further confirmed the high stability of the P3 polymer confined between the conductive MXene layers. When compared with those of the other organic materials composed of various carbons and other 2D materials, P3@Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} exhibited excellent cycling performance (Table S1). This is due to aligned and well-confined polymer chains between the highly conductive Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} layers, which is a favorable electrode architecture for ionic and electronic transport.\textsuperscript{31,22} The excellent cycling capability of the MXene-based polymer hybrids indicates that MXene helps to overcome the poor cycling of the organic materials, allowing sustainable long-term energy storage applications. It is important to point out that pristine Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} also offers good cycling stability.\textsuperscript{5,6}

\section*{Conclusions}

We have synthesized polyfluorene derivatives P1 [poly(9,9'-dioctylfluorene), poly({9,9′-bis[3"- (N,N-dimethylamino)propyl]-2,7-fluorene}-alt-2,7-(9,9′-dioctylfluorene))], P2 [poly-\{(9,9′-bis[3"- (N,N-dimethylamino)propyl]-2,7-fluorene}-alt-2,7-(9,9′-dioctylfluorene))], and P3 [poly\{(2,7-(9,9′-dioctylfluorene)}-alt-2,7-[9,9′-bis(5′-trimethylammonium bromide)-pentyl]fluorene\}] with different lateral chain functionalities to understand the interaction chemistry of a representative member of the MXene family, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}. Characterization using X-ray diffraction and various spectroscopic tools suggests that polymers bearing charged nitrogen-containing groups (P3)
juxtapose with Ti₃C₂Tₓ layers, hence expanding the interlayer spacing better than nonpolar (P1) and polar but neutral (P2) polymers. TEM results showed that the P3 polymer is confined between the Ti₃C₂Tₓ layers. A strong shift in FTIR and XPS peaks suggests that charged ends of the polymers play a crucial role in chemical interaction with MXene surfaces and most likely assist in the intercalation process. The P3@Ti₃C₂Tₓ hybrid exhibited improved gravimetric capacitance and a very high volumetric capacitance, along with excellent capacitance retention at both low and high scan rates. We attribute this to the improved accessibility of the MXene surface to protons due to pillaring of the Ti₃C₂Tₓ layers by polymer chains. The results presented here may guide the design of new organic—inorganic hybrid materials with well-defined properties for high-capacity energy storage applications and beyond. We stress that low-molecular weight polymers with redox functionalities can assist in the intercalation process and provide a high redox capacitance for energy storage applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b03933.

Experimental details, fluorescence microscopy images, XRD patterns, FTIR and XPS spectra, and the electrochemical performance of the hybrids (PDF)

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