

Supporting Information

Interaction of polar and non-polar polyfluorenes with layers of 2D titanium carbide (MXene): Intercalation and pseudocapacitance

Muhammad Boota,[†] Mariacecilia Pasini,[‡] Francesco Galeotti,[‡] William Porzio,[‡] Meng-Qiang Zhao,[†] Joseph Halim[†] and Yury Gogotsi^{†,}*

[†] A.J. Drexel Nanomaterials Institute and Department of Material Science and Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, Pennsylvania 19104, United States

[‡] Istituto per lo Studio delle Macromolecole, Consiglio Nazionale delle Ricerche (ISMAR-CNR), via Corti 12, 20133 Milano, Italy

***Corresponding author:**

Y. Gogotsi (gogotsi@drexel.edu) Tel.: +1-215-895-6446 Fax: +1-215-895-1934

Experimental Section

The Ti₃C₂T_x colloidal suspensions were synthesized similar to our previous reports.^{1,2} Briefly, 1 g lithium fluoride was slowly added to 20 mL 9 M hydrochloric acid solution followed by addition of 1 g of Ti₃AlC₂ powder. The reaction was allowed to occur under stirring for 24 h at 35 °C. The product was then washed with deionized water until a pH value of ~6 was reached. The delamination of the etched powder was achieved by 1 h bath sonication followed by 1 h centrifugation at 3500 rpm. The supernatant was decanted for further processing (2.1 mg/ml).

All the polymers were synthesized and characterized similar to previous reports.^{3,4} Briefly, for P1: A mixture of 2,7-dibromo-9,9'-dioctylfluorene (165 mg, 0.3 mmol), 9,9'-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (168 mg, 0.3 mmol), Pd(PPh₃)₄ (7 mg, 0.006 mmol), degassed aqueous potassium carbonate (2 M, 2.5 mL), and toluene (5 mL) was introduced in a Schenk tube under nitrogen atmosphere. The reaction mixture was stirred for 8 h at 80 °C. Then the end groups were capped by stirring the mixture at 80 °C for 8 h in excess of bromobenzene (0.4 mmol) and for further 8 h in excess of phenylboronic acid pinacol ester (0.4 mmol). After cooling to room temperature, the organic phase was precipitated in 200 mL of methanol to afford the product as white-yellow powder with a yield of 75%. For P2: A mixture

of 2,7-dibromo-9,9'-bis(3''-(*N,N*-dimethylamino)propyl)fluorene (150 mg, 0.3 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (168 mg, 0.3 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.003 mmol), degassed aqueous potassium carbonate (2 M, 6 mL), and THF (12 mL) was introduced in a Schenk tube under nitrogen atmosphere. The reaction mixture was stirred for 1 h at 70 °C. Then the end groups were capped by stirring the mixture at 70 °C for 2 h in excess of bromobenzene (0.4 mmol) and for further 2 h in excess of phenylboronic acid pinacol ester (0.4 mmol). After cooling to room temperature, the organic phase was precipitated in 200 mL of methanol to afford the product as green-yellow powder with a yield of 60%. For P3: A mixture of 2,7-dibromo-9,9'-bis(6''-bromohexyl)fluorene (100 mg, 0.16 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (899 mg, 0.16 mmol), PdCl₂(PPh₃)₂ (1 mg, 0.0015 mmol), degassed aqueous potassium carbonate (2 M, 1.5 mL), and THF (3 mL) was introduced in a Schenk tube under nitrogen atmosphere. The reaction mixture was stirred for 4 h at 70 °C. The end groups were capped by additional 4 h reaction in excess of bromobenzene (0.16 mmol) and further 4 h in excess of phenylboronic acid pinacol ester (0.16 mmol). After cooling to room temperature, the organic phase was precipitated in 150 mL of methanol to afford the neutral precursor polymer with a yield of 81%. The cationic polymer was obtained by trimethylamine ionization of the neutral precursor. Twelve milliliters of a 1:2 v/v solution of condensed trimethylamine in THF were added dropwise to a stirring solution of the neutral precursor polymer (100 mg) in 10 mL of THF at -78 °C. The mixture was then allowed to warm up to room temperature and then stirred overnight. After the solvent was removed, the salified polymer was recovered as a white powder in quantitative yield. The weight average molecular weight (M_w) and its distribution (M_w/M_n) were, respectively, 63 kDa and 2.76 for P1 and 99 kDa and 2.81 for P3. To prepare hybrid films, P1 and P2 were dissolved in 10 mL

chloroform while P3 was dissolved in the same volume of dimethyl sulfoxide (DMSO). The vacuum filtered $\text{Ti}_3\text{C}_2\text{T}_x$ films were dispersed in 10 mL DMSO to make a colloidal solution in three different 50 mL vials. After 20 minutes of sonication, each polymer solution was poured into separate $\text{Ti}_3\text{C}_2\text{T}_x$ vials and named according to the polymer added. The mass ratios between polymers and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes were controlled as 1: 2. All solutions were stirred up to 24 h at room temperature before solutions were vacuum filtered.⁵ The films were dried under vacuum up to 48 h, and then weighed to determine the polymer content in the hybrid films using an electronic balance. These films were further used for other characterizations.

The morphology of the hybrid films was investigated using a SEM (Zeiss Supra 50VP, Germany) and a TEM (JEOL JEM-2100, Japan) with an accelerating voltage of 200 kV. The TEM analyses on hybrid films were performed by first embedding films into epoxy resin, and then cutting them by a glass microtome followed by deposition on a lacey carbon coated copper grid. The XRD patterns were recorded on a Rigaku Smart Lab (Tokyo, Japan) diffractometer using Cu K α radiation (step scan = 0.02°, 2 Θ range= 3°– 80°, and step time = 0.5s). The XPS analysis was performed on a Physical Electronics Versa Probe 5000 (ULVAC-PHI, Inc., Japan) spectrometer using Al-K α monochromatic X-rays of 100 μm . An attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) with a resolution of 4 cm^{-1} was used to collect all the FTIR spectra. Renishaw inVia spectrometer (632 nm) was used to record all the Raman spectra (5% laser power).

All the electrochemical tests were performed in a three-electrode Swagelok cell with platinum current collectors on both sides in 1 M H_2SO_4 . A polypropylene disk ($d = 12$ mm) was used as a separator (Celgard 3501, Celgard LLC) and reference electrode was Ag/AgCl in 3 M KCl solution. The thickness of all the tested films was ~ 5 μm . The density of the $\text{P3@Ti}_3\text{C}_2\text{T}_x$

hybrid films was 2.70 g/cm^3 with an areal mass loading of 1.1 mg/cm^2 . The counter electrode was overcapacitive activated carbon (YP-50, Kuraray, Japan) mixed with 5 wt.% polytetrafluoroethylene ($d = 9 \text{ mm}$, thickness $\approx 100 \text{ }\mu\text{m}$). All the electrochemical tests were performed using VMP3 potentiostat (BioLogic, France). The specific capacitances were calculated by integrating the discharge portions of the CVs.^{1,6} The galvanostatic charge/discharge tests were conducted between the potential limits of -0.2 to 0.4 V vs. Ag/AgCl reference electrode.

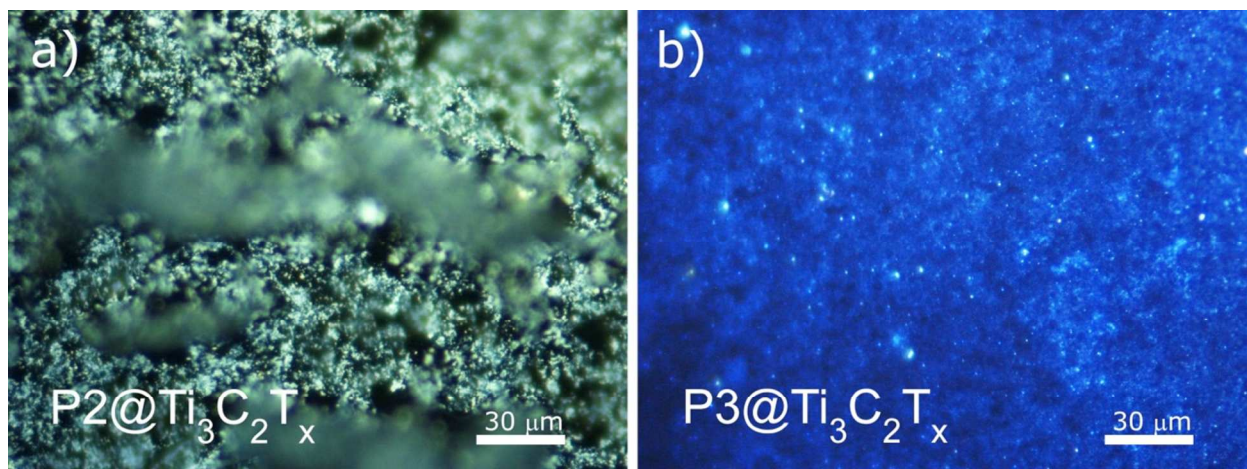


Figure S1: Fluorescence microscopy images of (a) $\text{P2@Ti}_3\text{C}_2\text{T}_x$, and (b) $\text{P3@Ti}_3\text{C}_2\text{T}_x$.

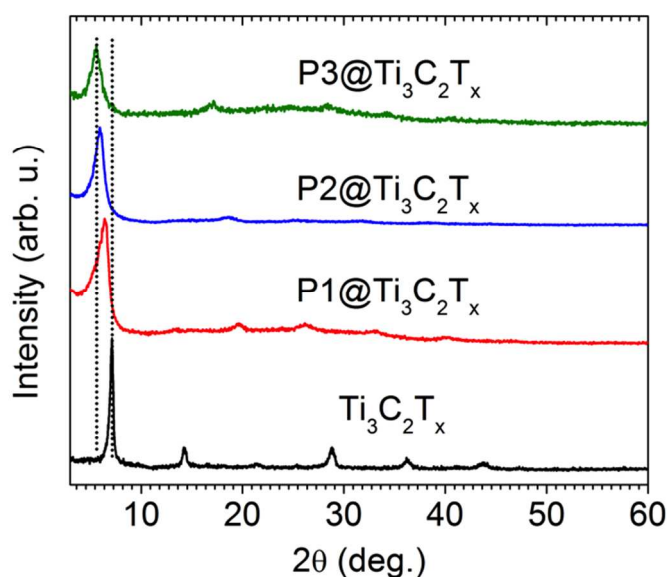


Figure S2: XRD patterns of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and its hybrids at higher 2θ angles.

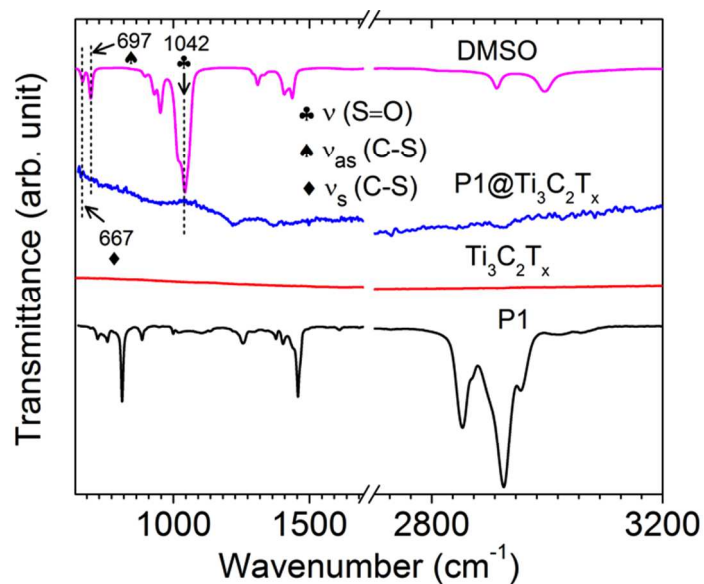


Figure S3: FTIR spectra of P1, pristine $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{P1@Ti}_3\text{C}_2\text{T}_x$ and DMSO.

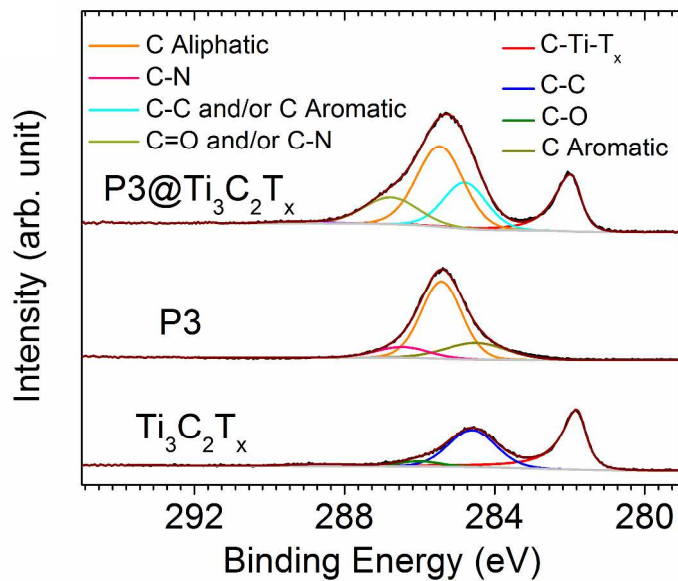


Figure S4: XPS spectra of the C1s region for $\text{Ti}_3\text{C}_2\text{T}_x$, P3 and $\text{P3@Ti}_3\text{C}_2\text{T}_x$ hybrid.

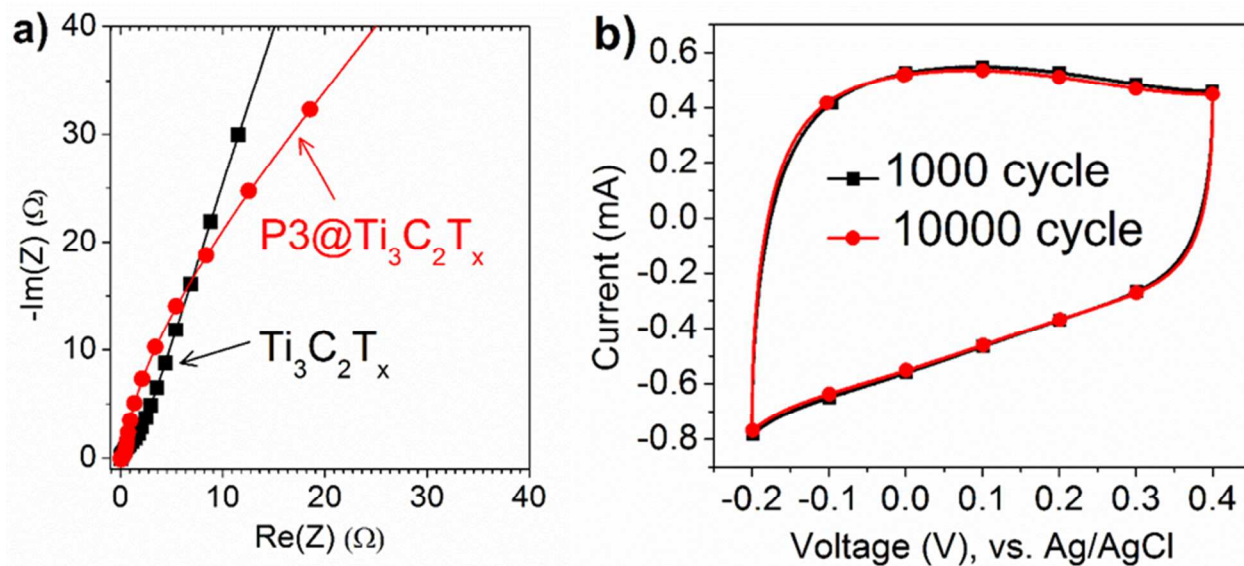


Figure S5: a) Enlarged high-frequency region of the Nyquist plot. b) Identical CV curves before and after long cycling, which confirm the high electrochemical stability of the confined P3 polymer chains between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers.

Table S1: Cycling stability of the organic hybrid materials in comparison with the P3@Ti₃C₂T_x material.

Reported electrode material	Electrolyte	Scan rate or current density	Cycling stability (% retention after cycles)	Ref.
PANI paper/Graphene	1 M H ₂ SO ₄	5 A/g	82 (1000)	7
PANI nanofibers/Graphene	1 M H ₂ SO ₄	3 A/g	79 (800)	8
MoS ₂ /PPy	1 M H ₂ SO ₄	1 A/g	90 (500)	9
CNT/PPy-NW	1 M KCl	1 A/g	85 (1000)	10
Carbon nanofoam/PEDOT	0.1 M LiClO ₄	1 A/g	14 (10000)	11
PQ/OLC	1 M H ₂ SO ₄	200 mV/s	90 (10000)	12
Catechol/AC	1 M H ₂ SO ₄	7.5 A/g	75 (10000)	13
PPy/Ti ₃ C ₂ T _x	1 M H ₂ SO ₄	100 mV/s	92 (25000)	14
PANI/MOF	1 M H ₂ SO ₄	1 A/g	90 (100)	15
MoS ₂ /PANI	1 M H ₂ SO ₄	3 A/g	79 (6000)	16
HQ/Graphene	1 M H ₂ SO ₄	10 A/g	86 (10000)	17
MoS ₂ /PPy	1 M KCl	1 A/g	85 (4000)	18
MoO ₃ /PANI	1 M H ₂ SO ₄	20 mV/s	50 (200)	19
		20 mV/s	100 (3000)	Current work
P3@Ti₃C₂T_x	1 M H₂SO₄	100 mV/s	98 (10000)	

References

- (1) Ghidui, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive Two-Dimensional Titanium Carbide Clay with High Volumetric Capacitance. *Nature* **2014**, *516*, 78–81.
- (2) Ren, C. E.; Zhao, M.; Makaryan, T.; Halim, J.; Boota, M.; Kota, S.; Anasori, B.; Barsoum, M. W.; Gogotsi, Y. Porous Two-Dimensional Transition Metal Carbide (MXene) Flakes for High-Performance Li-Ion Storage. *ChemElectroChem* **2016**, *3*, 689–693.
- (3) Castelli, A.; Meinardi, F.; Pasini, M.; Galeotti, F.; Pinchetti, V.; Lorenzon, M.; Manna, L.; Moreels, I.; Giovanella, U.; Brovelli, S. High-Efficiency All-Solution-Processed Light-Emitting Diodes Based on Anisotropic Colloidal Heterostructures with Polar Polymer Injecting Layers. *Nano Lett.* **2015**, *15*, 5455–5464.
- (4) Leone, G.; Giovanella, U.; Galeotti, F.; Barba, L.; Arrighetti, G.; Scavia, G.; Rapallo, A.; Porzio, W. Conjugated Dye-Intercalated Fluoromica Hybrids Displaying Tunability of Optical Properties through Packing Variation. *Dye. Pigment.* **2016**, *124*, 53–62.
- (5) Ling, Z.; Ren, C. E.; Zhao, M.-Q.; Yang, J.; Giammarco, J. M.; Qiu, J.; Barsoum, M. W.; Gogotsi, Y. Flexible and Conductive MXene Films and Nanocomposites with High Capacitance. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 16676–16681.
- (6) Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall'Agnese, Y.; Rozier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide. *Science*. **2013**, *341*, 1502–1505.
- (7) Cong, H.-P.; Ren, X.-C.; Wang, P.; Yu, S.-H. Flexible Graphene–polyaniline Composite Paper for High-Performance Supercapacitor. *Energy Environ. Sci.* **2013**, *6*, 1185.
- (8) Wu, Q.; Xu, Y.; Yao, Z.; Liu, A.; Shi, G. Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films. *ACS Nano* **2010**, *4*, 1963–1970.
- (9) Ma, G.; Peng, H.; Mu, J.; Huang, H.; Zhou, X.; Lei, Z. In Situ Intercalative Polymerization of Pyrrole in Graphene Analogue of MoS₂ as Advanced Electrode Material in Supercapacitor. *J. Power Sources* **2013**, *229*, 72–78.
- (10) Fu, H.; Du, Z.; Zou, W.; Li, H.; Zhang, C. Carbon Nanotube Reinforced Polypyrrole Nanowire Network as a High-Performance Supercapacitor Electrode. *J. Mater. Chem. A* **2013**, *1*, 14943–14950.
- (11) Sidhu, N. K.; Rastogi, A. C. Electrochemical Performance of Supercapacitors Based on Carbon Nanofoam Composite and Microporous poly(3, 4-Ethylenedioxythiophene) Thin Film Asymmetric Electrodes. *Mater. Chem. Phys.* **2016**, *176*, 75–86.
- (12) Zeiger, M.; Weingarth, D.; Presser, V. Quinone-Decorated Onion-Like Carbon/Carbon Fiber Hybrid Electrodes for High-Rate Supercapacitor Applications. *ChemElectroChem* **2015**, *2*, 1117–1127.
- (13) Pognon, G.; Cougnon, C.; Mayilukila, D.; Bélanger, D. Catechol-Modified Activated Carbon Prepared by the Diazonium Chemistry for Application as Active Electrode Material in Electrochemical Capacitor. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3788–3796.
- (14) Boota, M.; Anasori, B.; Voigt, C.; Zhao, M.-Q.; Barsoum, M. W.; Gogotsi, Y. Pseudocapacitive Electrodes Produced by Oxidant-Free Polymerization of Pyrrole between the Layers of 2D Titanium Carbide (MXene). *Adv. Mater.* **2015**, *28*, 1517–1522.
- (15) Guo, S.; Zhu, Y.; Yan, Y.; Min, Y.; Fan, J.; Xu, Q.; Yun, H. (Metal-Organic Framework)-Polyaniline Sandwich Structure Composites as Novel Hybrid Electrode Materials for High-Performance Supercapacitor. *J. Power Sources* **2016**, *316*, 176–182.
- (16) Ren, L.; Zhang, G.; Yan, Z.; Kang, L.; Xu, H.; Shi, F.; Lei, Z.; Liu, Z.-H. Three-Dimensional Tubular MoS₂/PANI Hybrid Electrode for High Rate Performance Supercapacitor. *ACS Appl. Mater. Interfaces* **2015**, *7*, 28294–28302.
- (17) Xu, Y.; Lin, Z.; Huang, X.; Wang, Y.; Huang, Y.; Duan, X. Functionalized Graphene Hydrogel-Based High-Performance Supercapacitors. *Adv. Mater.* **2013**, *25*, 5779–5784.
- (18) Tang, H.; Wang, J.; Yin, H.; Zhao, H.; Wang, D.; Tang, Z. Growth of Polypyrrole Ultrathin Films on MoS₂ Monolayers as High-Performance Supercapacitor Electrodes. *Adv. Mater.* **2015**, *27*, 1117–1123.
- (19) Xia, X.; Hao, Q.; Lei, W.; Wang, W.; Wang, H.; Wang, X. Reduced-Graphene Oxide/molybdenum Oxide/polyaniline Ternary Composite for High Energy Density Supercapacitors: Synthesis and Properties. *J. Mater. Chem.* **2012**, *22*, 8314.