

Supporting Information

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

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Experimental Section

The $Ti_3C_2T_x$ 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 Ti_3AlC_2 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), $Pd(PPh_3)_4$ (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 P3@ $\text{Ti}_3\text{C}_2\text{T}_x$

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.

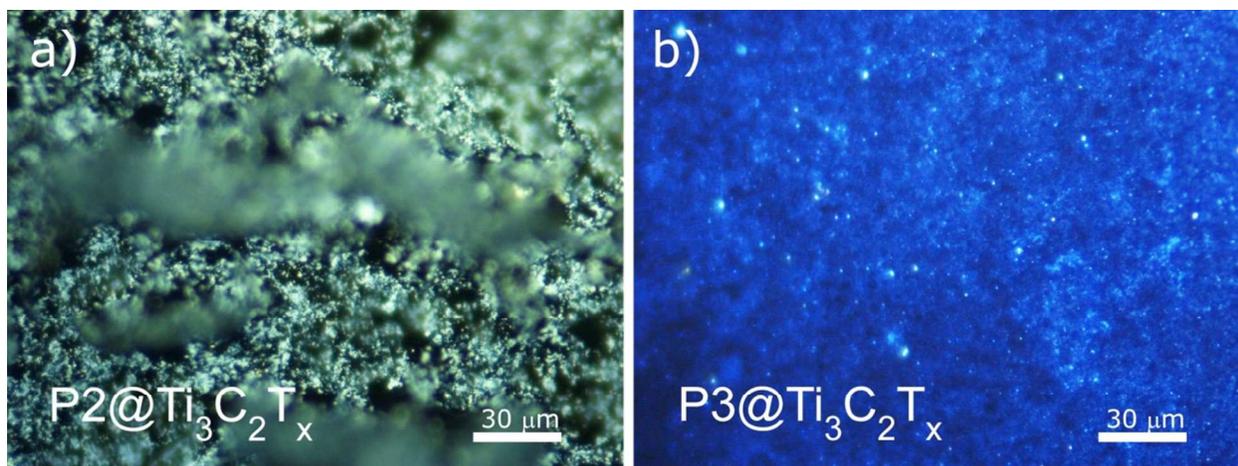


Figure S1: Fluorescence microscopy images of (a) $\text{P2@Ti}_3\text{C}_2\text{T}_x$, and (b) $\text{P3@Ti}_3\text{C}_2\text{T}_x$.

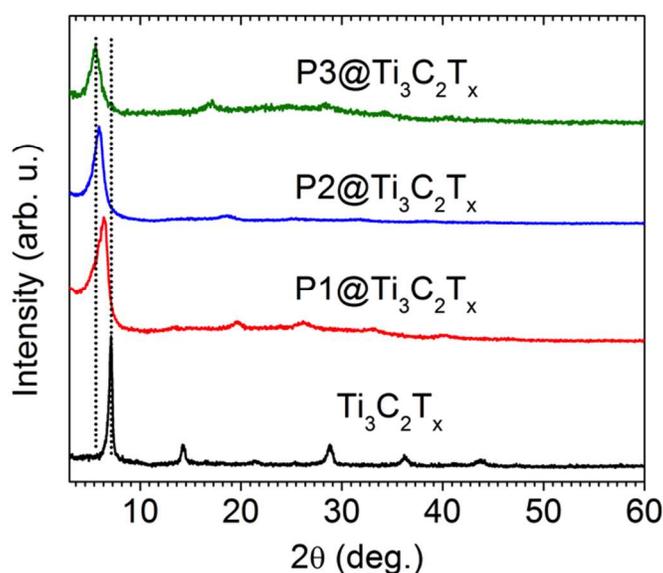


Figure S2: XRD patterns of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and its hybrids at higher 2θ angles.

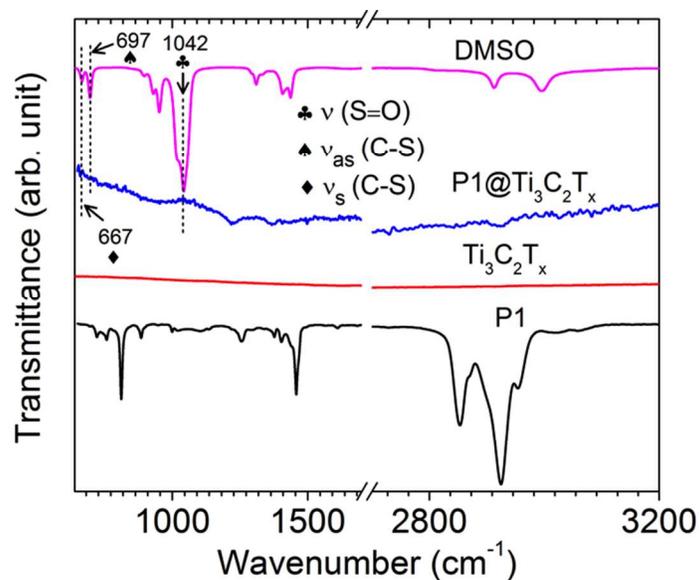


Figure S3: FTIR spectra of P1, pristine $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{P1@Ti}_3\text{C}_2\text{T}_x$ and DMSO.

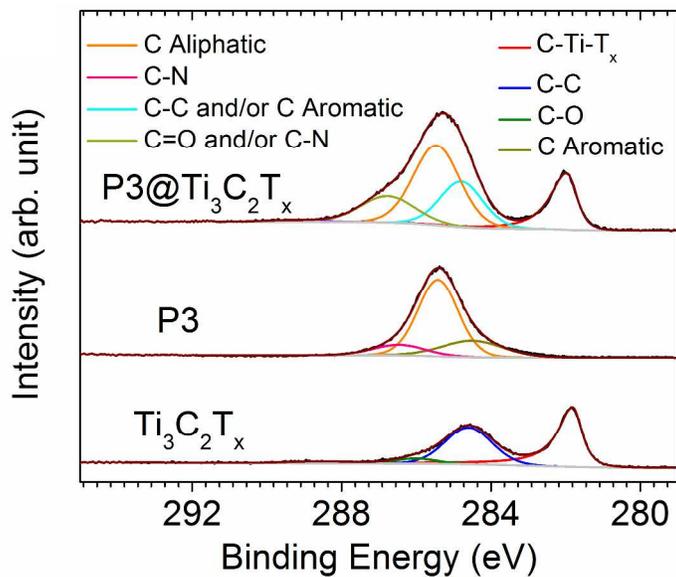


Figure S4: XPS spectra of the C1s region for $\text{Ti}_3\text{C}_2\text{T}_x$, P3 and $\text{P3@Ti}_3\text{C}_2\text{T}_x$ hybrid.

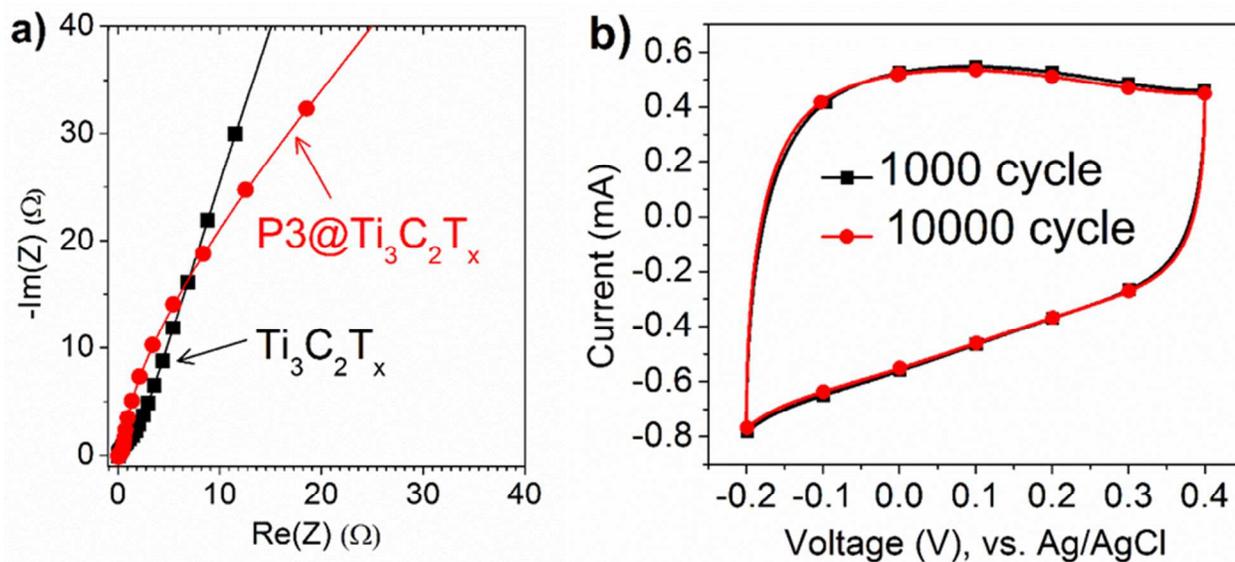


Figure S5: a) Enlarged high-frequency region of the Nyquist plot. b) Identical CV curves before and after long cycling, which confirm the high electrochemical stability of the confined P3 polymer chains between the $\text{Ti}_3\text{C}_2\text{T}_x$ layers.

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
P3@Ti₃C₂T_x	1 M H₂SO₄	100 mV/s	98 (10000)	Current work

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