Supporting Information

Coupling Porphyrin with MXene Nanosheets: Exploring Non-Covalent Interactions and Photophysical Characteristics

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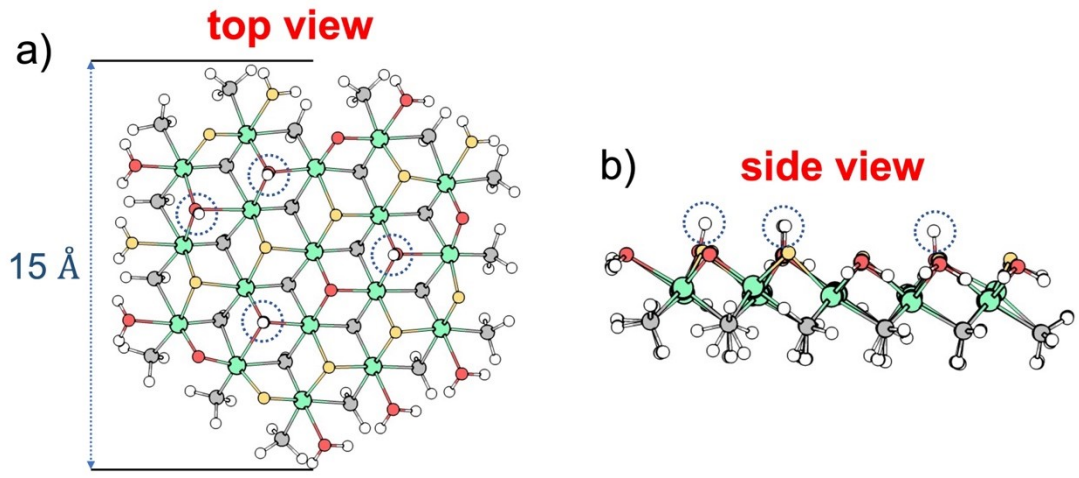


Fig. S1. $Ti_{18}C_{26}O_{14}H_{72}F_{12}$ cluster model used in calculations: a) top and b) side views. Hydrogen atoms active in optimizations are marked with blue circles.

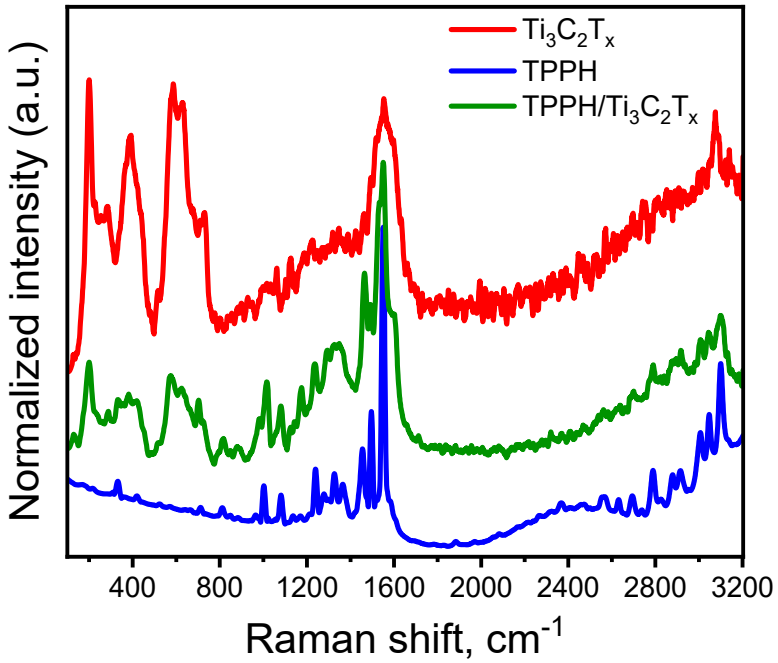


Fig. S2. Raman spectra of the TPPH, $Ti_3C_2T_x$ and the TPPH/$Ti_3C_2T_x$ nanohybrid in the range of 100 to 3200 cm^{-1}.

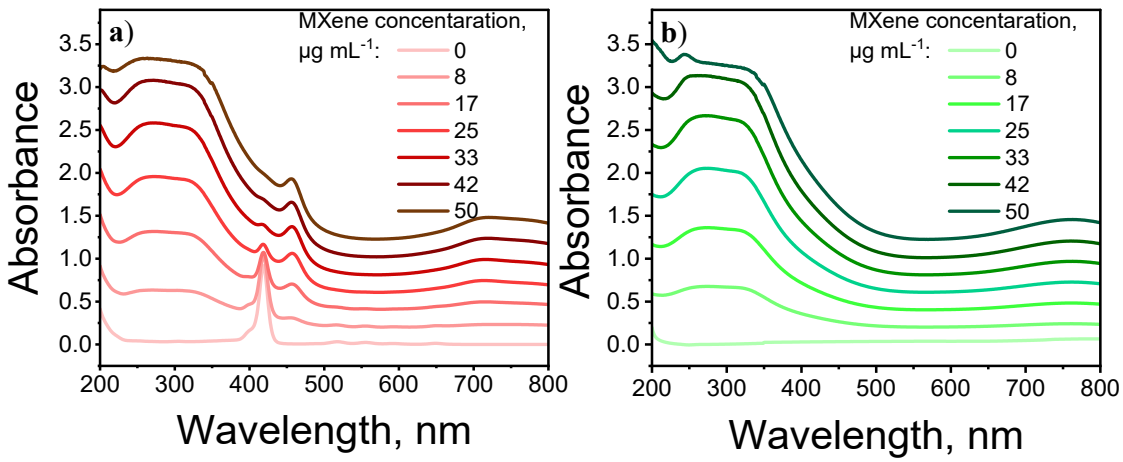


Fig. S3. Absorption spectra recorded during the process of titration with 1.25 mg mL^{-1} of $Ti_3C_2T_x$ dispersion of a) 3 mL of EtOH-H_2O (1:2 v/v) solution of 2.2 μM TPPH, b) 3 mL of EtOH-H_2O (1:2 v/v) solution.

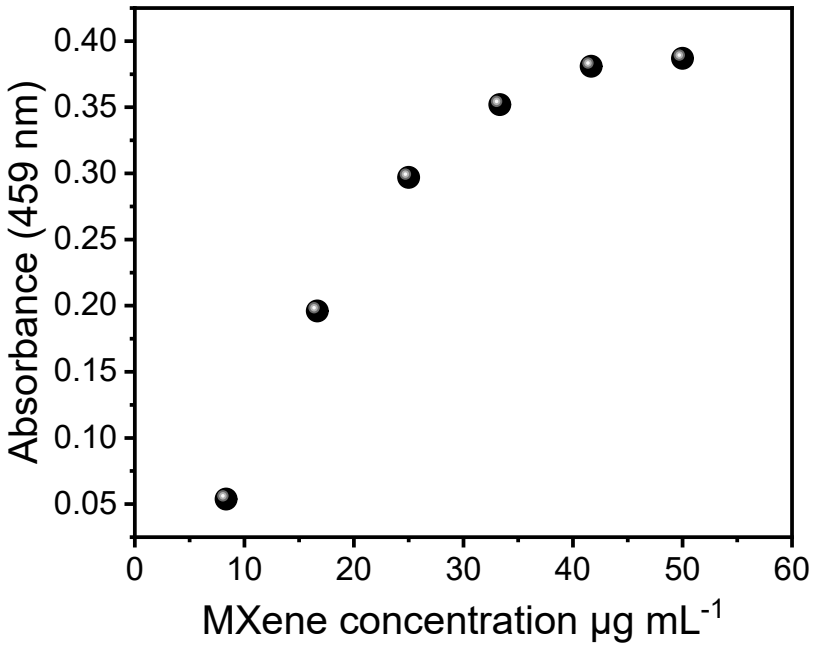


Fig. S4. Absorbance changes at 459 nm upon addition of $Ti_3C_2T_x$ to the TPPH solution in EtOH-H_2O (1:2 v/v).

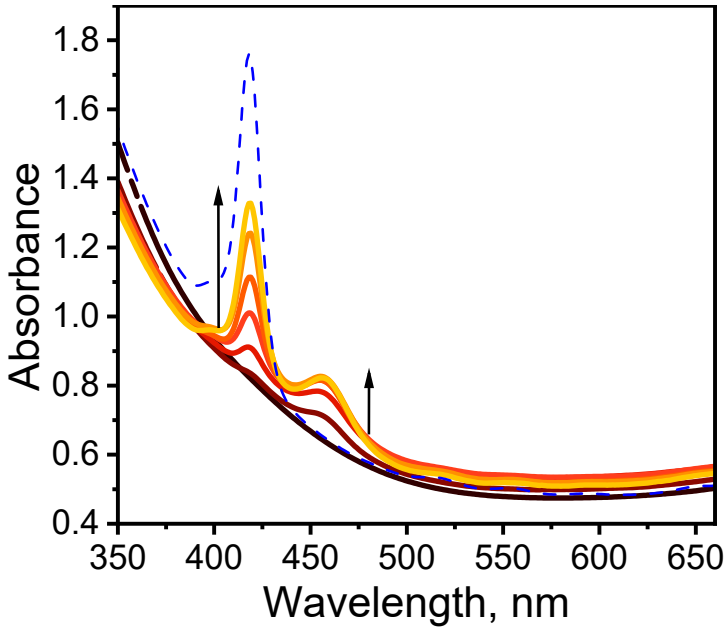


Fig. S5. Absorption spectra recorded during the process of titration of 3 ml of 0.33 mg mL^{-1} of $Ti_3C_2T_x$ EtOH-H_2O (1:2 v/v) dispersion with solution of TPPH (0 – 2.2 μM), the dotted blue line represents the mathematical sum of the absorption of $Ti_3C_2T_x$ (0.33 mg mL^{-1}) and TPPH (2.2 μM).

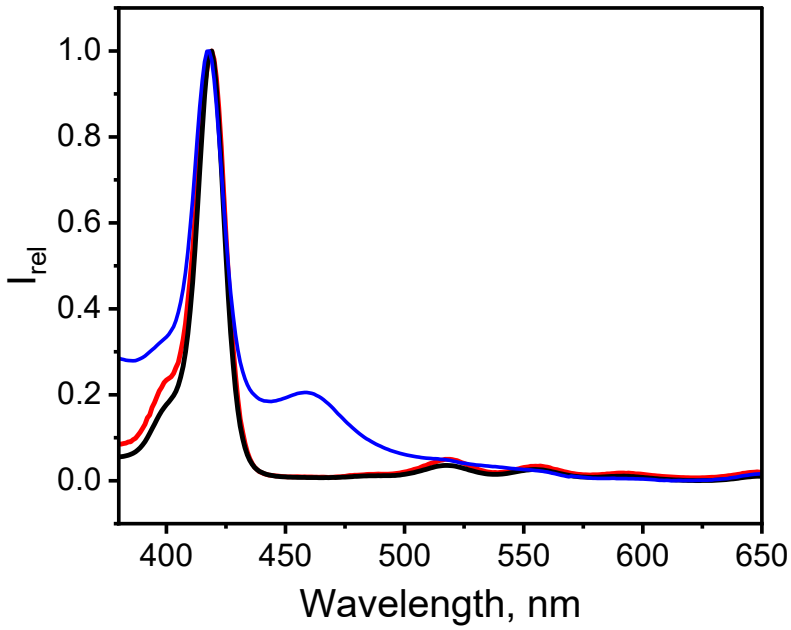


Fig. S6. Normalized fluorescence excitation spectrum of the mixture of TPPH (1.3 μM) and $Ti_3C_2T_x$ (12 μg mL^{-1}) (red), normalized absorption spectrum of this mixture (blue) and normalized absorption spectrum of TPPH (1.3 μM) in the absence of $Ti_3C_2T_x$ (black).

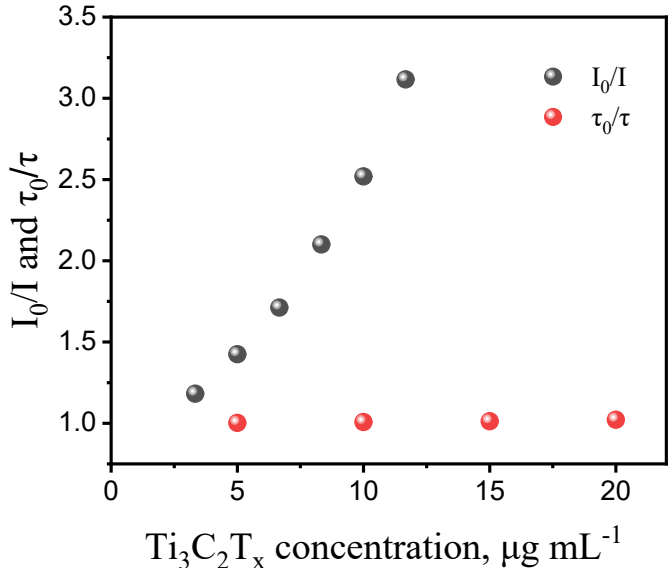


Fig. S7. The relationship between fluorescence intensity I_0/I (black symbols) (I_0 – I_f without $Ti_3C_2T_x$, I – I_f after addition of $Ti_3C_2T_x$) and $Ti_3C_2T_x$ concentration and the relationship between fluorescence lifetime τ_0/τ (red symbols) (τ_0 – fluorescence lifetime without $Ti_3C_2T_x$, τ – fluorescence lifetime after addition of $Ti_3C_2T_x$) and $Ti_3C_2T_x$ concentration for TPPH. Data corrected for inner filter effect.

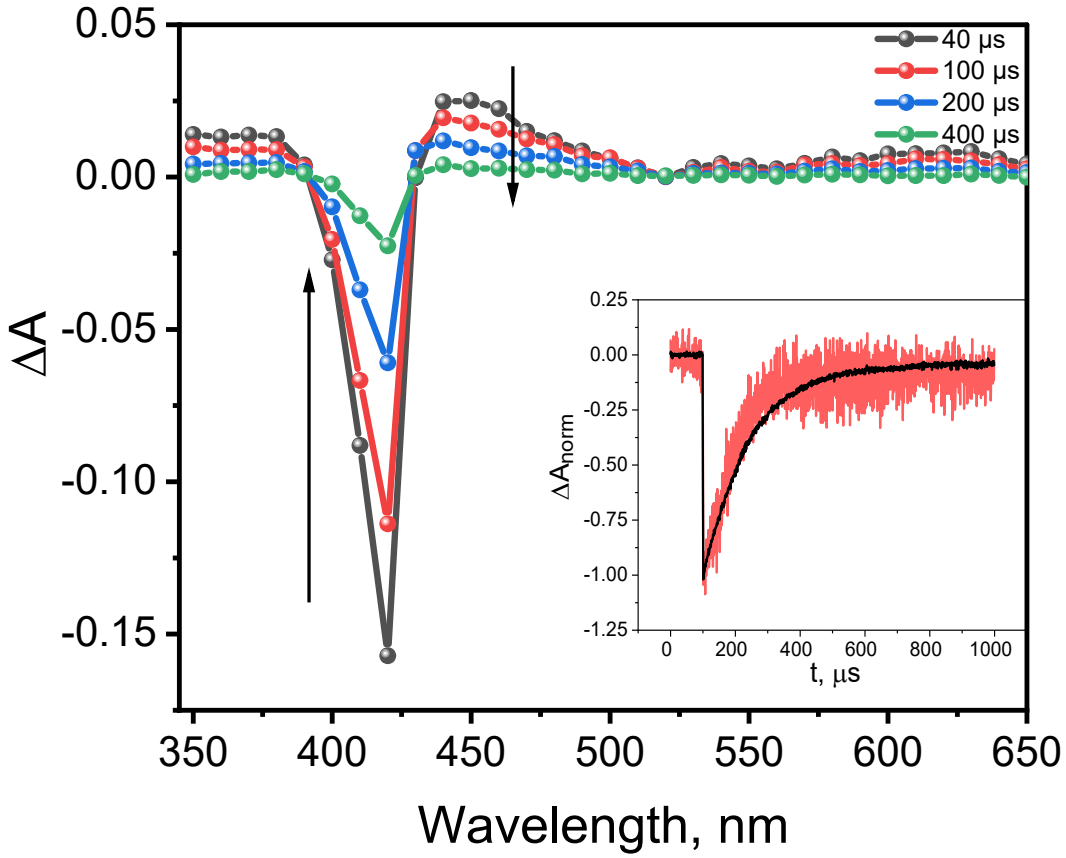
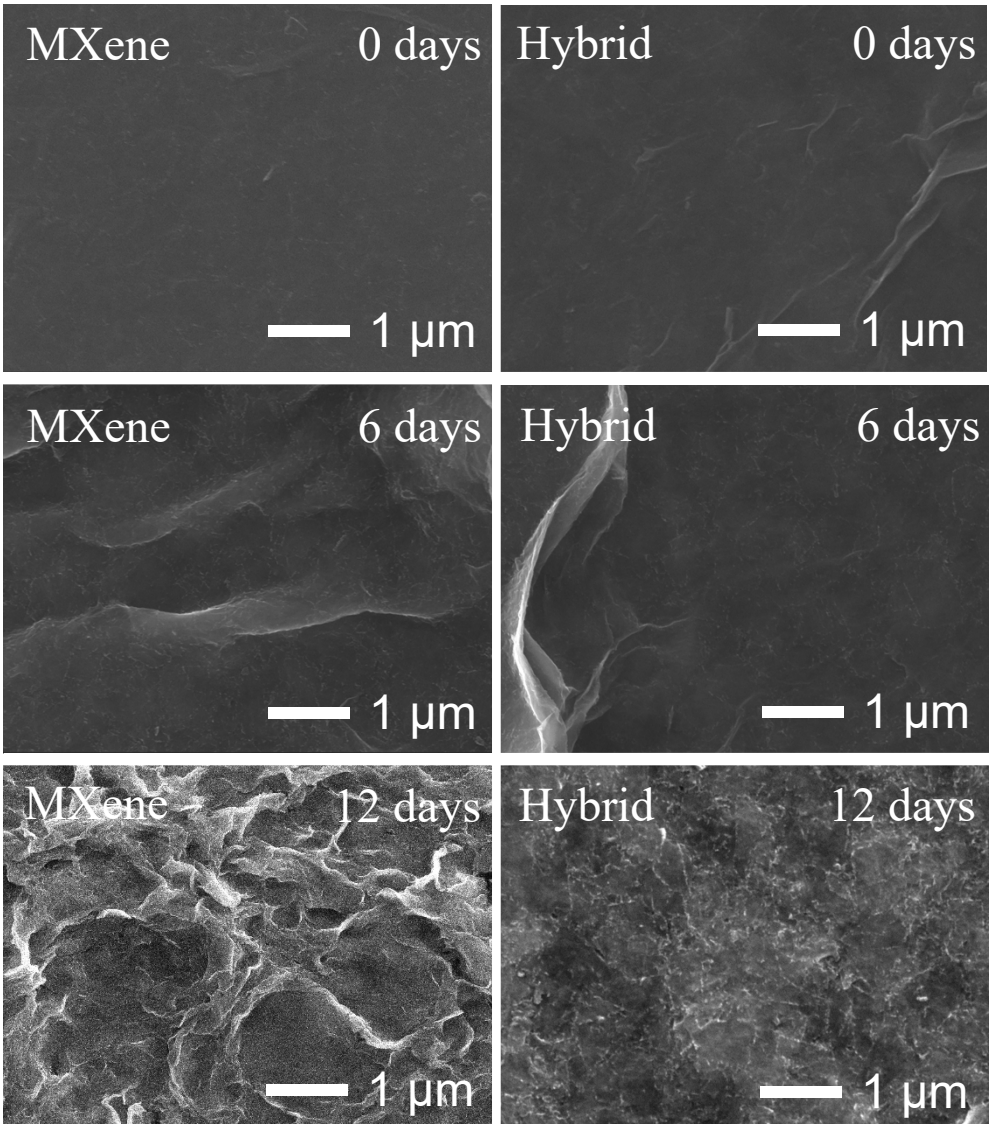


Fig. S8. Transient absorption spectra obtained during laser flash photolysis with excitation at 355 nm of deoxygenated solutions of TPPH (5 μM) in EtOH-H_2O (1:2 v/v) after different time delays. Inset: Normalized profiles of bleach recovery monitored at 420 nm obtained during nanosecond laser flash photolysis (with excitation at 355 nm) of deoxygenated solutions of TPPH (5 μM) (black) and for TPPH in the presence of $Ti_3C_2T_x$ (5 μg mL^{-1}) (red).

Stability test

We present the observations recorded on the day of colloidal solution preparation, as well as on



the sixth and twelfth days thereafter.

Fig. S9. SEM images of $Ti_3C_2T_x$ (left column) and TPPH/$Ti_3C_2T_x$ (right column) colloidal solutions captured on day 0 (immediately after preparation), day 6, and day 12.

From those micrographs, one can notice the gradual edge oxidation (day 6) of MXene flakes composing Si-deposited MXene's thin layer, which is more pronounced in the case of the MXene pristine sample. Further aging of the colloidal solutions led to additional decomposition of the material and the formation of disordered carbon.

Raman spectroscopy enabled us to monitor oxidation-induced changes in the colloidal solutions over time. In addition to the characteristic vibrational modes, we observed an increase in intensity within the carbon-related region of the $Ti_3C_2T_x$ Raman spectra, specifically between 1000 and 1600 cm^{-1} (Fig. S10). This enhancement is indicative of structural transformations in the carbon framework, such as an increased presence of disordered carbon structures or oxidation products, aligning with findings from previous studies on oxidative weathering effects on carbonaceous materials.[1] Throughout the oxidation trials, no Raman peaks characteristic of anatase TiO_2, particularly the ~150 cm^{-1} Eg mode, were observed, indicating that significant formation of TiO_2 nanoparticles did not occur under the experimental conditions. It's important to note that the formation of anatase is often associated with more advanced stages of oxidation, which may require longer exposure times or more aggressive oxidative environments.

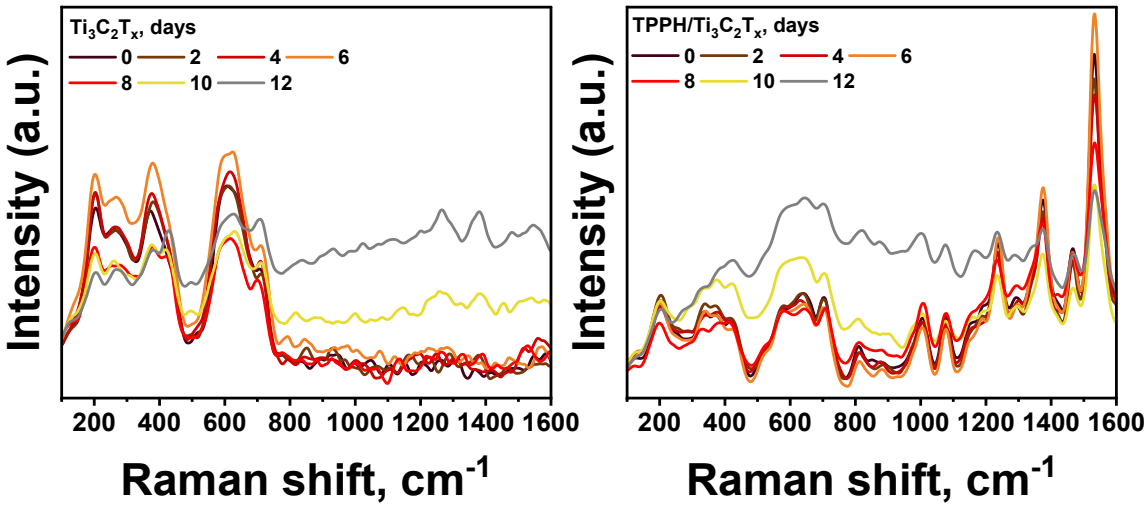


Fig. S10. Raman spectra of fresh and aged $Ti_3C_2T_x$ and TPPH/$Ti_3C_2T_x$ colloidal solutions for different durations of time.

The observed changes in zeta potential for the MXene colloidal solution indicate a significant alteration in surface charge over time. Initially, the pristine $Ti_3C_2T_x$ colloidal solution exhibited a zeta potential of -37 mV, while its hybrid counterpart (TPPH/$Ti_3C_2T_x$) measured at -41 mV, revealing a very strong electrostatic repulsion between the dispersed particles.[2] After storage under ambient conditions, these values shifted to -23 mV and -28 mV, respectively (Figure S11).

This reduction in negative zeta potential suggests a decrease in colloidal stability, likely due to oxidation processes affecting the surface functional groups of the MXene flakes. Oxidation can lead to the formation of less negatively charged or neutral species on the MXene surface, diminishing electrostatic repulsion between particles and promoting aggregation. The more pronounced change in the pristine MXene colloidal solution implies that the presence of TPPH in the hybrid may offer some protective effect against oxidation, possibly by interacting with reactive sites or providing a barrier to environmental factors.

To the best of our knowledge, XRD is infrequently employed to monitor the degradation processes of MXenes.[3, 4] In our study, we conducted XRD analyses up to the sixth day of observing the degradation of both pristine $Ti_3C_2T_x$ and its hybrid with TPPH (Figure S12).

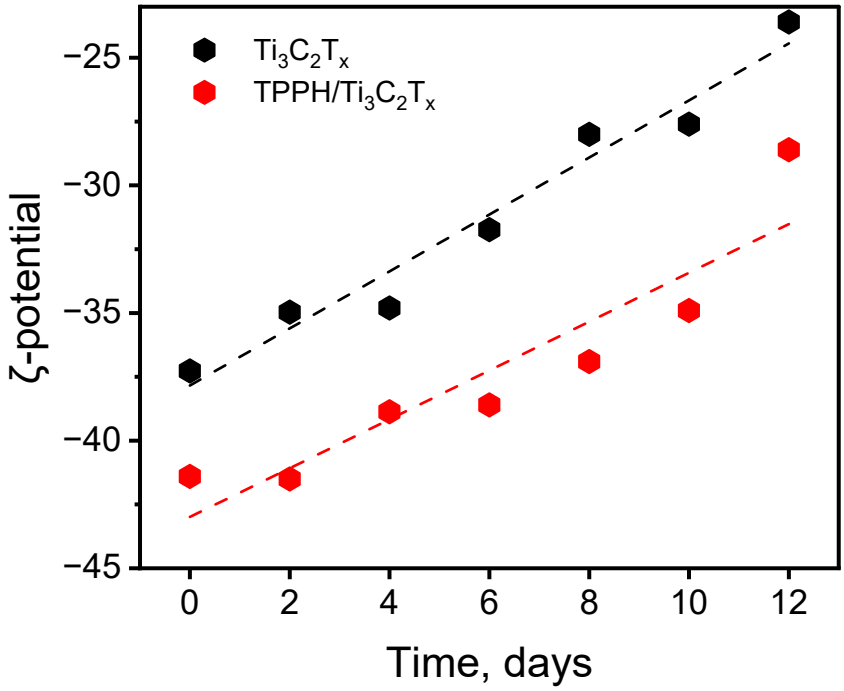


Fig. S11. Temporal changes in zeta-potential of pristine $Ti_3C_2T_x$ and TPPH/$Ti_3C_2T_x$ colloidal solutions under ambient conditions. The lines represent linear fitting results: black for $Ti_3C_2T_x$ and red for TPPH/$Ti_3C_2T_x$, their corresponding slope values are 1.12 and 0.96.

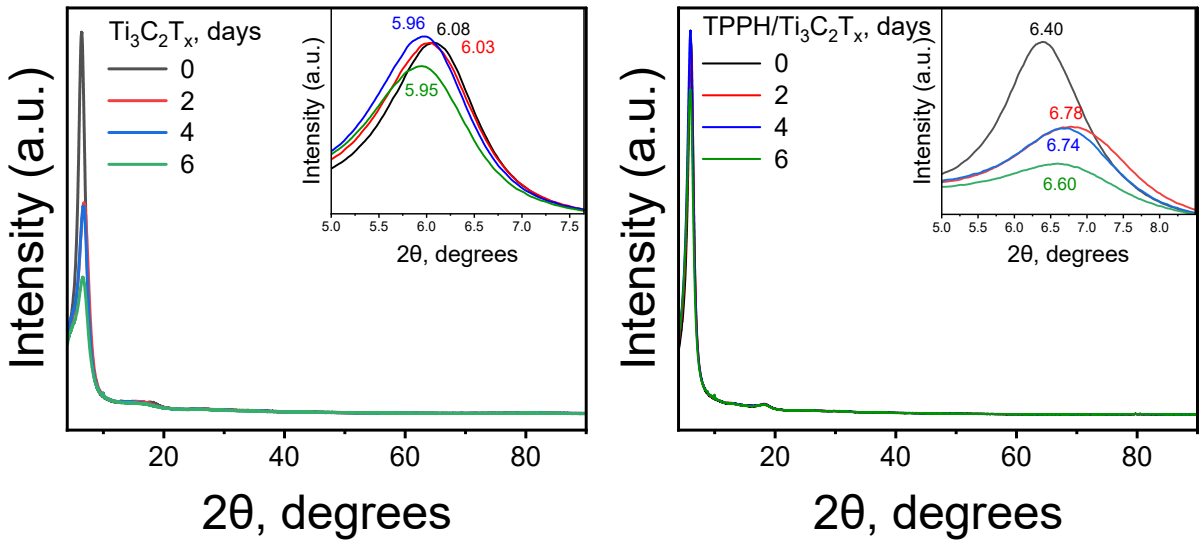


Fig. S12. XRD patterns of $Ti_3C_2T_x$ and TPPH/$Ti_3C_2T_x$ colloidal solutions recorded on the day of preparation and subsequently every other day up to day 6. Inset: magnified view of the (002) diffraction peaks.

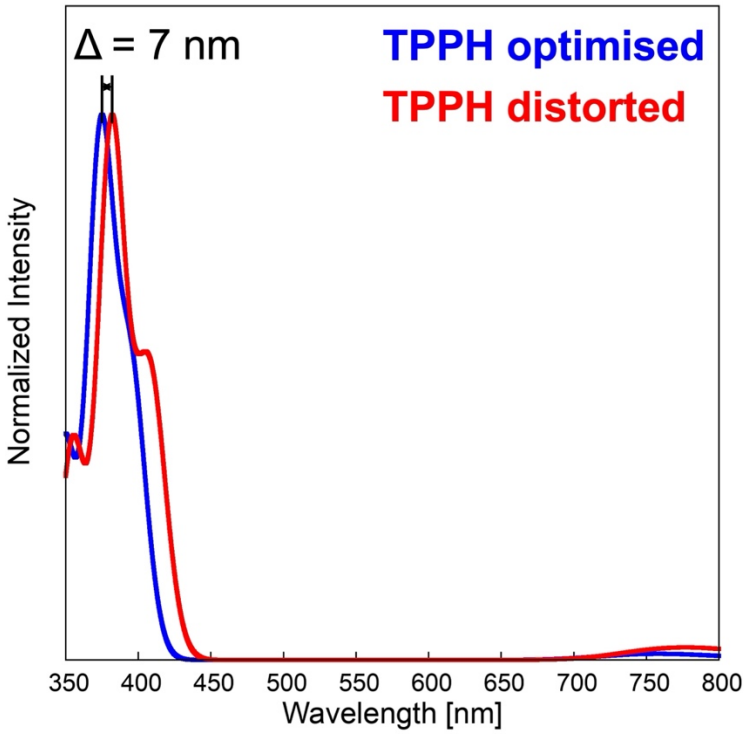


Fig. S13. Simulated UV-Vis spectra of TPPH optimised in the gas phase (blue line, structure shown in main manuscript Figure 10a) and distorted TPPH molecule as found in the TPPH/$Ti_3C_2T_x$ system (red line, structure shown in main manuscript Figure 10c). Highlighted is the shift of the Soret band.

Cartesian coordinates of molecules discussed in the manuscript

TPPH

C	1.99787137017697	0.02011400177467	-36.14747321570749
C	-1.88837929046420	-2.96854806961333	-35.78955425262491
C	-4.89602033112177	0.96798453101614	-35.63771323820275
C	-1.00971714350241	3.95643483239851	-36.00047628065069
N	-3.13267597183517	-0.80079396450875	-35.75035858492344
N	-0.20434542044208	-1.13453164709756	-35.94155737577308
N	0.23266585188127	1.78863781986903	-36.06660063301354
N	-2.69200828491851	2.12335375244797	-35.81780797642988
C	0.16874318084291	3.16861285558790	-35.99639313090034
C	1.54834099946874	1.36189643562249	-36.06402481780619
C	1.15499063964159	-1.12811471716982	-36.14410459794147
C	-0.57320825532424	-2.45772567940868	-35.98539774286490

C	-2.33776694739764	3.44191753707454	-35.97494609807485
C	-4.06628759969909	2.11254133872791	-35.81370459954203
C	-4.43412703483767	-0.37039430558136	-35.56516699478600
C	-3.05450962477690	-2.17704374929823	-35.63600076532845
C	1.52983939136653	3.64540342342979	-35.92104263352994
C	2.36971710519037	2.54543935213623	-35.96224133676078
C	1.66432016783657	-2.48792489612534	-36.36574288442647
C	0.58143853231667	-3.32099825490085	-36.26675591706805
C	-4.38652131791821	-2.64626210524830	-35.33433649831903
C	-5.22640816509144	-1.54636773961013	-35.29073086083502
C	-3.52412319587270	4.29576360605961	-36.11881827208546
C	-4.60715568996303	3.46275670138931	-36.01846779290624
H	1.81794072597313	4.70075006014297	-35.82526290408158
H	3.46632071655182	2.54137288954547	-35.90515974785956
H	2.70409744386004	-2.76036428676859	-36.59517032413001
H	0.55761507818346	-4.41179709811671	-36.39929211937373
H	-4.65234492278927	-3.69598640836897	-35.15203194851316
H	-6.30147045510986	-1.53731293601187	-35.06708536346412
H	-3.52303297213286	5.37901594197284	-36.30481148356662
H	-5.67024302425281	3.72769721128728	-36.10583017419106
C	3.47658284021312	-0.18738775618981	-36.23972640288214
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C	4.18047194681035	-0.88216941487693	-35.22397989325144
H	3.69232144740494	0.83263724532676	-38.15491609884689
H	3.62379833727780	-1.26349723540257	-34.34963093116748
C	5.60609647737450	0.10602629180325	-37.42974081314067
C	5.56615586413327	-1.08126769569238	-35.29857845604213
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H	6.10788637140230	-1.61557552837895	-34.49879969718142
C	6.29304328383648	-0.58747363567779	-36.40675799342118
C	-2.07240735645806	-4.45210703790340	-35.73610248620807
C	-1.45886732457919	-5.22905218438842	-34.72127305094749
C	-2.86264987439033	-5.12558265229286	-36.69724962622008
H	-0.84650796610496	-4.72362017341648	-33.95359464827548
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C	-1.62498143566990	-6.61987591934264	-34.66318239614637
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H	-1.15060792471421	-7.21635483730185	-33.86455038444959
H	-3.64815070571153	-7.02287125714764	-37.42407963953209
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C	-6.37227404970377	1.17533034045386	-35.51336954827614
C	-6.91443106594847	1.92456960408740	-34.44245807229115
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C	-8.65839816362741	0.82008050749000	-36.35133687734569
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O	-10.54303198957328	1.72701101406330	-35.20914500086814
H	-10.76085985523259	2.26658458499548	-34.42046741293910
O	-2.54583623743657	-8.63797010172446	-35.53381473919076
H	-3.11565896682464	-8.95479736295760	-36.26560273684946
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O	-0.27826124220961	9.62106448898424	-36.14826244754062
H	-0.64782807537685	10.03880159638883	-35.34233775144839

$Ti_{18}C_{26}O_{14}H_{72}F_{12}$ cluster model

C	-7.59474998999035	-2.63089987887006	-29.64568976304601
C	-4.55685034710200	-2.63090024589500	-29.64569095557563
F	-6.07581994845784	-3.50786010857101	-31.85609993306393
Ti	-6.06000751199487	-1.54123449571659	-30.61204944840656
C	-9.11370001963452	-0.00000035149892	-29.64569023167155
C	-6.07579994455029	-0.00000022105758	-29.64568968838188
F	-7.32010086256382	-0.86013427230709	-32.02072204449607
Ti	-7.46533473672058	0.91337338528277	-30.67371055323441
C	-7.59475029902229	2.63090034655580	-29.64568993304950
O	-9.11371008911241	1.75393992303380	-31.85609997630921
C	-3.03790006260837	-5.26180000677478	-29.64568990303747
C	-0.00000008952647	-5.26179978833097	-29.64569013683656
O	-1.51896002863014	-6.13875001999097	-31.85610002492912
Ti	-1.58426082959056	-4.21377256367207	-30.78973785245328
C	-1.51894979562853	-2.63090015463514	-29.64568966119354
O	-2.99401075566894	-3.44070437561302	-31.83846193954780
Ti	-3.07547624021285	-1.90507133320906	-30.79716721849804
C	-3.03789975041237	-0.00000001780291	-29.64568958669411
O	-4.55503658647323	-0.84918087674209	-31.98867692916264
Ti	-4.33442024754536	0.85046931226587	-30.70627761556532
C	-4.55685031803135	2.63090021278822	-29.64569023405703
O	-6.20910895303884	1.92310435426257	-32.02183637371888
Ti	-5.83400487075860	3.47410933660695	-30.61273751585438
C	-6.07579983415392	5.26179992517711	-29.64568992434719
F	-7.59476018264512	4.38483988493261	-31.85609996495987
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F	1.51893001108418	-6.13875003933943	-31.85610000795651
Ti	1.55825089573710	-4.13806049542559	-30.66960865999041
C	1.51895008897088	-2.63090012131562	-29.64568995930713
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F	-1.43772124120851	-0.85879758516129	-31.98373651507197
Ti	-1.37971860363846	0.91448003838707	-30.75415583764316
C	-1.51894994956139	2.63089992826328	-29.64568996789866
F	-3.07835410543008	1.70387148592098	-32.02673433052767
Ti	-2.88869076224498	3.56586305356020	-30.64076316583726
C	-3.03789980709335	5.26179995944879	-29.64568987015373
F	-4.66140558749083	4.33701233764018	-32.03302738152117
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O	2.82278107330470	-3.41835784654227	-31.89911334461984
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O	1.39475705115662	-0.84628772368378	-31.98362498026976
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C	1.51895008032652	2.63089988666449	-29.64568997890151
O	-0.01225495785930	1.74786297581207	-31.79696704089840
Ti	0.02969287503947	3.43125549263031	-30.73194809504945
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O	-1.57050038098568	4.22018466663943	-31.99813069494628
C	6.07580002896790	0.00000000193992	-29.64568999403191
F	4.35970260478443	-0.73423792488588	-32.08961011183722
Ti	4.45419590070456	0.76709208425558	-30.68195441931777
C	4.55684994999519	2.63090002098343	-29.64569002796383
F	3.01436610525955	1.76563803830201	-31.98822710947434
Ti	2.99012911113257	3.48172931857490	-30.57312833663781
C	3.03790001741849	5.26179999939317	-29.64569003555617
F	1.54313385151872	4.33653222420410	-31.98484778344347
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H	0.78891631079435	-6.60450982556929	-31.54537858243194

$Ti_{18}C_{26}O_{14}H_{72}F_{12}$ + TPPH

C	-7.594750000	-2.630900000	-29.645690000
C	-4.556850000	-2.630900000	-29.645691000
F	-6.075820000	-3.507860000	-31.856100000
Ti	-6.061214000	-1.539725000	-30.612759000
C	-9.113700000	0.000000000	-29.645690000
C	-6.075800000	0.000000000	-29.645690000
F	-7.352742000	-0.926900000	-32.010177000
Ti	-7.458248000	0.928053000	-30.669658000
C	-7.594750000	2.630900000	-29.645690000
O	-9.113710000	1.753940000	-31.856100000
C	-3.037900000	-5.261800000	-29.645690000
C	0.000000000	-5.261800000	-29.645690000
O	-1.518960000	-6.138750000	-31.856100000
Ti	-1.573518000	-4.217511000	-30.763527000
C	-1.518950000	-2.630900000	-29.645690000
O	-3.017073000	-3.459675000	-31.835008000
Ti	-3.090396000	-1.907270000	-30.817288000
C	-3.037900000	0.000000000	-29.645690000
O	-4.565885000	-0.865198000	-31.991623000
Ti	-4.340705000	0.848223000	-30.730128000
C	-4.556850000	2.630900000	-29.645690000
O	-6.178676000	1.887901000	-31.999901000
Ti	-5.827231000	3.472819000	-30.624166000
C	-6.075800000	5.261800000	-29.645690000
F	-7.594760000	4.384840000	-31.856100000
C	3.037900000	-5.261800000	-29.645690000
F	1.518930000	-6.138750000	-31.856100000
Ti	1.557939000	-4.142371000	-30.660522000
C	1.518950000	-2.630900000	-29.645690000
F	0.006443000	-3.581893000	-32.007920000
Ti	0.009165000	-1.671167000	-30.656725000
C	0.000000000	0.000000000	-29.645690000
F	-1.437322000	-0.879676000	-31.981473000
Ti	-1.394294000	0.921020000	-30.758505000
C	-1.518950000	2.630900000	-29.645690000
F	-3.041822000	1.703313000	-31.999447000
Ti	-2.874787000	3.574445000	-30.675392000
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F	-4.629689000	4.334087000	-32.008172000
C	4.556850000	-2.630900000	-29.645690000
O	2.819445000	-3.413930000	-31.898615000
Ti	3.154579000	-1.892915000	-31.000319000
C	3.037900000	0.000000000	-29.645690000
O	1.400760000	-0.828582000	-31.962889000
Ti	1.500574000	0.883848000	-30.722734000
C	1.518950000	2.630900000	-29.645690000
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Ti	0.024282000	3.427000000	-30.769612000
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C	6.075800000	0.000000000	-29.645690000
F	4.357049000	-0.724684000	-32.095374000
Ti	4.450564000	0.762402000	-30.684020000
C	4.556850000	2.630900000	-29.645690000
F	3.036159000	1.795614000	-31.986345000
Ti	2.990847000	3.465978000	-30.576439000
C	3.037900000	5.261800000	-29.645690000
F	1.546566000	4.343647000	-31.976541000

Ti	-4.330320000	6.171562000	-30.808337000
Ti	-1.519269000	6.285177000	-30.937435000
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H	-11.629529000	-0.290326000	-36.025498000

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