Supporting Information

Mechanochemical Construction 2D/2D Covalent Organic Nanosheets Heterojunctions based on Sub-stoichiometric Covalent Organic Frameworks

Yongliang Yang[a,b], Weijia Zhao[a,b], Hongyun Niu[a], Yaqi Cai[a,c,d]*

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Institute of Environment and Health, Jianghan University, Wuhan 430056, China

[d] Institute of Environment and Health , Hangzhou Institute for Advanced Study, UCAS

* Corresponding author: E-mail: caiyaqi@rcees.ac.cn; Fax: +86-10-6284-9182; Tel.: +86-10-6284-9239.

Section S1 General Information

1.1 Chemicals and reagents

All reagents and solvents were purchased from commercial sources and used without further purification. 3,3′,5,5′-tetramethylbenzidine (TMB), triethanolamine (TEOA), p-benzoquinone (BQ), p-toluenesulfonic acid (PTSA) solution (12 wt % in acetic acid solution) were purchased from J&K Chemical Co. Ltd. Sulfamethazine (SMT) was purchased from Acros Organics. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), tert-butanol (t-BuOH) were obtained from Sinopharm Chemistry Reagent Co. Ltd. Melamine monomer was purchased from TCI. 1,3,6,8-tetrakis(p-formylphenyl) pyrene, 2,4,6-trimethyl-1,3,5-triazine, 1,3,5-triformylphloroglucinol were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd.

1.2 Characterization

Powder X-ray diffraction (PXRD, Bruker D8 ADVANCE, Germany) using a Cu Kα (λ = 1.5418 Å) radiation ranging from 5 °to 40 °with a resolution of 0.02 °was utilized to analysis the crystalline. The microstructures of the catalysts were investigated by field emission scanning electron microscope (FE-SEM, Quattro ESEM, Thermo Fisher) and high-resolution transmission electron microscope (HR-TEM, JEM-2100F, JEOL) at accelerating voltage of 200 kV. Atomic force microscope (AFM) images were taken with a Bruker Dimension Icon instrument in the tapping mode. Surface analysis by X-ray photoelectron spectroscopy (XPS) was carried out using Thermo Fisher ESCALAB 250Xi equipment (Waltham, MA), and the X-ray source was Al Kα radiation (1486.6 eV, monochromatic). Fourier transform-infrared (FT-IR) spectra in the 4000–400 cm^{-1} region were recorded on a NEXUS 670 Infrared Fourier Transform Spectrometer (Nicolet Thermo, Waltham, MA). Solid-state nuclear magnetic resonance (ssNMR) spectroscopy was obtained on a JNM-ECZ600R spectrometer (JEOL). Elemental analysis (EA) was conducted on an EA3000 analyzer (EUROVECTOR). Surface area and pore volume were measured by BrunauerEmmett-Teller (BET) methods

(ASAP2000 V3.01A; Micrometritics, Norcross, GA). The diffuse reflectance spectra (DRS) were collected using a Hitachi U-3900 UV–vis spectrophotometer ($BaSO_4$ as a reflectance standard). The electron spin resonance (ESR) spectrum was detected by a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. High performance liquid chromatography analysis was carried out on an Dionex SUMMIT® HPLC system (Dionex, Sunyvale, CA) with a PDA-100 photodiode array detector, Dikma C18 column (5 μm, 4.6 mm × 150 mm). The mobile phase was composed of acetonitrile/water (25:75) containing 0.05% acetic acid. The wavelength was set at 265 nm, and the flow rate was 1.0 $mL.min^{-1}$ with a column temperature of 30 ℃. Visible-light irradiation was provided by a CEL-HXF300F3 300 W xenon lamp (CEAULIGHT).

1.3 Photoelectrochemical measurements

All photoelectrochemical measurements were investigated on a CHI760E electrochemical analyzer (Chenhua, Shanghai, China) in a standard three-electrode system, using a platinum foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The electrolyte was a 0.2 $mol \cdot L^{-1}$ Na_2SO_4 aqueous solution. The working electrodes were prepared as follows: The 2 mg of catalyst was added into 1 mL of methanol and 10 μL of Nafion mixed solution. Then a 100 μL suspension was dropped on the surface of a indium tin oxide (ITO) glass substrate and dried at room temperature for photocurrent measurements. A 300 W xenon lamp with a UV cutoff filter (>420 nm) was used as the light source in photocurrent measurements. Mott-Schottky curves were measured at a frequency of 1 kHz. Electrochemical impedance spectroscopy (EIS) frequency ranged from 1 to 10^6 Hz with an AC voltage magnitude of 10 mV.

Section S2 Structure modeling and characterization

Structural modeling of PTO-COF was generated using the Accelrys Materials Studio 7.0 software package. The space groups were obtained from the Reticular Chemistry Structure Resource. The model was constructed in the initial lattice with the space group of P1. The proposed model was geometry optimized using the MS Forcite molecular

dynamics module (Universal force fields, Ewald summations) to obtain the optimized lattice parameters. The stagger stacking of PTO-COF was examined by offsetting the stacked units from the AA model. Pawley refinement was applied to define the lattice parameters by Reflex module, producing the refined PXRD profiles.

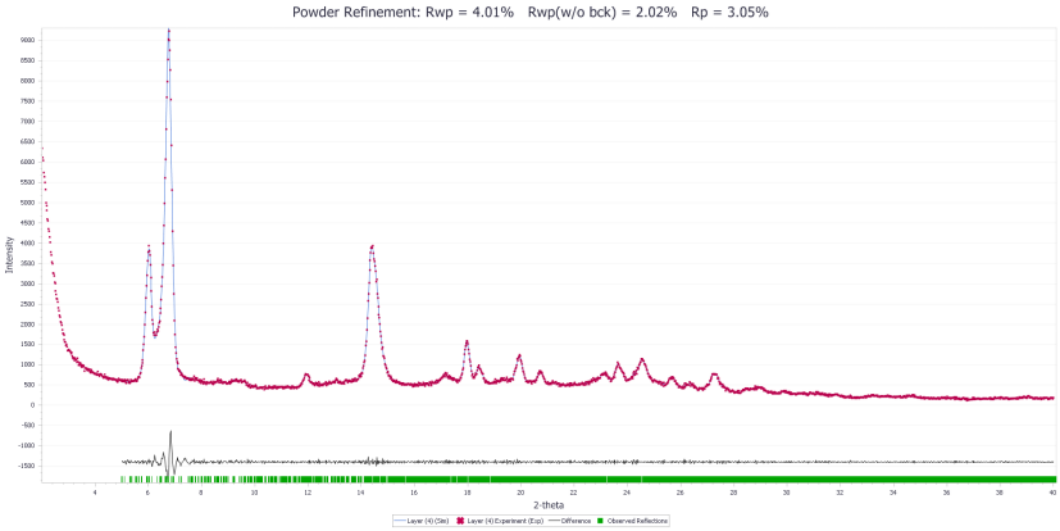

Figure S1. Pawley refinement of PTO-COF.

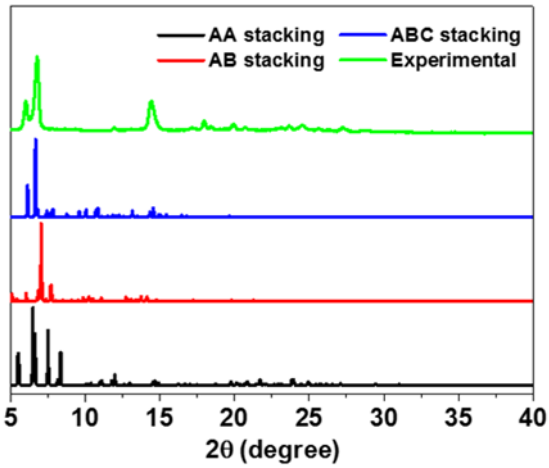

Figure S2. The experimental and simulated PXRD patterns.

Table S1. Atomistic coordinates for the Pawley-refined PTO-COF

PTO-COF	**P1** **a = 18.30 Å, b= 40.19 Å, c=51.73 Å** **α = 65.34°, β = 115.93°, γ = 88.86°**		
Atom	x	y	z
C1	0.53748	0.53348	0.17081
C2	0.55584	0.49667	0.17447
C3	0.64009	0.47488	0.19311
C4	0.7056	0.49	0.20772

C5	0.6866	0.52598	0.20407
C6	0.60424	0.54839	0.18558
C7	0.45342	0.55463	0.15143
C8	0.38904	0.53984	0.13697
C9	0.40571	0.50366	0.14028
C10	0.48997	0.48187	0.15892
C11	0.65677	0.43869	0.19642
C12	0.59239	0.4239	0.18196
C13	0.50833	0.44505	0.16259
C14	0.44157	0.43014	0.14783
C15	0.3592	0.45255	0.12933
C16	0.34021	0.48853	0.12567
C17	0.59346	0.58752	0.18158
C18	0.79557	0.47022	0.22575
C19	0.45235	0.39101	0.15184
C20	0.25024	0.50832	0.10763
C21	0.64755	0.60943	0.17445
C22	0.64354	0.64477	0.1732
C23	0.58472	0.65958	0.17861
C24	0.52936	0.63806	0.18518
C25	0.53501	0.6022	0.18721
C26	0.8298	0.43753	0.25608
C27	0.91577	0.42042	0.27371
C28	0.96873	0.43583	0.26131
C29	0.93434	0.46865	0.23096
C30	0.84852	0.48576	0.21341
C31	0.39831	0.36909	0.159
C32	0.40235	0.33373	0.16029
C33	0.46115	0.3189	0.15489
C34	0.51646	0.34044	0.14827
C35	0.51077	0.37632	0.1462
C36	0.21604	0.54101	0.0773
C37	0.13006	0.55813	0.05966
C38	0.07708	0.54272	0.07204
C39	0.11144	0.5099	0.10239
C40	0.19726	0.49279	0.11995
C41	0.58653	0.69672	0.17816
C42	0.53548	0.71485	0.18307
C43	0.54511	0.751	0.1835
N44	0.61015	0.76527	0.18134
C45	0.61742	0.79914	0.1804
N46	0.56005	0.81866	0.18215
C47	0.49599	0.80442	0.18509

N48	0.4882	0.77056	0.1856
C49	0.43456	0.82725	0.18608
C50	0.68788	0.81415	0.17801
C51	0.45939	0.28174	0.15538
C52	0.51043	0.2636	0.15048
C53	0.50086	0.22742	0.1501
N54	0.43586	0.21314	0.15229
C55	0.42864	0.17925	0.15327
N56	0.48602	0.15972	0.15154
C57	0.55004	0.17397	0.14856
N58	0.55778	0.20784	0.14802
C59	0.35821	0.16423	0.15569
C60	0.6115	0.15113	0.1476
C61	0.364	0.12708	0.16911
C62	0.67465	0.16292	0.14291
C63	0.37139	0.81545	0.19075
C64	0.68211	0.8513	0.1646
C65	0.05932	0.41753	0.2803
C66	0.9865	0.56103	0.05303
O67	0.10635	0.42968	0.26972
O68	0.93944	0.54889	0.0636
C69	0.95053	0.02736	0.16291
C70	0.0224	0.00706	0.16669
C71	0.09215	0.02284	0.16926
C72	0.09047	0.05852	0.16829
C73	0.01949	0.07827	0.16423
C74	0.94842	0.06406	0.16079
C75	0.88169	0.01106	0.1595
C76	0.88439	0.97569	0.16122
C77	0.954	0.95552	0.16448
C78	0.02375	0.9713	0.16704
C79	0.16176	0.00267	0.17252
C80	0.16446	0.9673	0.17424
C81	0.09561	0.951	0.17082
C82	0.09772	0.9143	0.17294
C83	0.02664	0.90009	0.1695
C84	0.95567	0.91984	0.16544
C85	0.87452	0.08916	0.15473
C86	0.15983	0.07729	0.16955
C87	0.17161	0.8892	0.17899
C88	0.88631	0.90107	0.16418
C89	0.85194	0.12849	0.13392
C90	0.78669	0.15231	0.13

C91	0.74106	0.13732	0.14609
C92	0.76355	0.09821	0.16683
C93	0.82987	0.07485	0.1713
C94	0.23997	0.06123	0.19723
C95	0.30612	0.07792	0.19712
C96	0.29233	0.11153	0.16981
C97	0.21132	0.1284	0.14262
C98	0.1456	0.11137	0.14252
C99	0.19416	0.84987	0.19978
C100	0.25938	0.82605	0.20368
C101	0.30501	0.84105	0.18759
C102	0.28255	0.88017	0.16688
C103	0.21626	0.90352	0.16243
C104	0.80616	0.91714	0.1365
C105	0.74	0.90046	0.1366
C106	0.75378	0.86684	0.16391
C107	0.83479	0.84997	0.1911
C108	0.90053	0.86699	0.1912
H109	0.73776	0.53687	0.21579
H110	0.43589	0.58355	0.14585
H111	0.32589	0.55755	0.12263
H112	0.71992	0.42099	0.21076
H113	0.60992	0.39498	0.18754
H114	0.30806	0.44166	0.11761
H115	0.6933	0.59914	0.16982
H116	0.68696	0.6606	0.16799
H117	0.4834	0.64791	0.18984
H118	0.49392	0.58579	0.19338
H119	0.79007	0.42553	0.26617
H120	0.94106	0.39528	0.29716
H121	0.97374	0.48123	0.22089
H122	0.82332	0.51128	0.19023
H123	0.35257	0.37938	0.16363
H124	0.35897	0.31789	0.16553
H125	0.5624	0.33058	0.14361
H126	0.55183	0.39273	0.14001
H127	0.25579	0.55301	0.06721
H128	0.1048	0.58326	0.0362
H129	0.07202	0.49733	0.11245
H130	0.22244	0.46727	0.14314
H131	0.63429	0.70966	0.17388
H132	0.486	0.70351	0.18691
H133	0.44213	0.85519	0.18256

H134	0.74476	0.79438	0.18676
H135	0.41168	0.26879	0.15969
H136	0.55986	0.27495	0.1466
H137	0.30131	0.184	0.14692
H138	0.60396	0.12318	0.15113
H139	0.42351	0.10733	0.18054
H140	0.67858	0.19182	0.13704
H141	0.36743	0.78657	0.1966
H142	0.6226	0.87105	0.15317
H143	0.08495	0.39284	0.30403
H144	0.96089	0.58572	0.0293
H145	0.02009	0.10546	0.16378
H146	0.82188	0.02613	0.15292
H147	0.82958	0.96494	0.159
H148	0.21658	0.01342	0.17474
H149	0.22428	0.95222	0.18082
H150	0.02604	0.87291	0.16994
H151	0.88452	0.14089	0.12049
H152	0.77127	0.18243	0.11411
H153	0.73294	0.08557	0.181
H154	0.84689	0.04537	0.18813
H155	0.25179	0.03515	0.21841
H156	0.36821	0.06453	0.21828
H157	0.19949	0.15395	0.121
H158	0.08399	0.12425	0.12105
H159	0.16158	0.83746	0.21321
H160	0.27478	0.79593	0.21955
H161	0.31317	0.89281	0.15271
H162	0.19926	0.93301	0.14561
H163	0.79436	0.94322	0.11532
H164	0.67792	0.91386	0.11544
H165	0.84661	0.82441	0.21272
H166	0.96213	0.8541	0.21267
C167	0.87078	0.86681	0.50414
C168	0.88914	0.83	0.50781
C169	0.97339	0.80821	0.52645
C170	0.0389	0.82333	0.54105
C171	0.0199	0.85931	0.5374
C172	0.93754	0.88172	0.51891
C173	0.78672	0.88796	0.48477
C174	0.72234	0.87317	0.4703
C175	0.73901	0.83699	0.47361
C176	0.82327	0.8152	0.49225

C177	0.99007	0.77202	0.52975
C178	0.92569	0.75723	0.51529
C179	0.84163	0.77838	0.49592
C180	0.77487	0.76347	0.48116
C181	0.6925	0.78588	0.46266
C182	0.67351	0.82186	0.459
C183	0.92676	0.92085	0.51492
C184	0.12887	0.80355	0.55908
C185	0.78565	0.72434	0.48517
C186	0.58354	0.84165	0.44096
C187	0.98085	0.94276	0.50779
C188	0.97684	0.9781	0.50653
C189	0.91802	0.99291	0.51194
C190	0.86266	0.97139	0.51851
C191	0.86831	0.93553	0.52054
C192	0.1631	0.77086	0.58941
C193	0.24907	0.75375	0.60704
C194	0.30203	0.76916	0.59464
C195	0.26764	0.80198	0.5643
C196	0.18182	0.81909	0.54675
C197	0.73161	0.70242	0.49233
C198	0.73565	0.66706	0.49363
C199	0.79445	0.65223	0.48822
C200	0.84976	0.67377	0.4816
C201	0.84407	0.70965	0.47954
C202	0.54934	0.87434	0.41063
C203	0.46336	0.89146	0.39299
C204	0.41038	0.87605	0.40538
C205	0.44474	0.84323	0.43572
C206	0.53056	0.82612	0.45328
C207	0.91983	0.03005	0.51149
C208	0.86878	0.04818	0.5164
C209	0.87841	0.08433	0.51683
N210	0.94345	0.0986	0.51467
C211	0.95072	0.13247	0.51374
N212	0.89335	0.15199	0.51548
C213	0.82929	0.13775	0.51843
N214	0.8215	0.10389	0.51893
C215	0.76786	0.16058	0.51941
C216	0.02118	0.14748	0.51134
C217	0.79269	0.61507	0.48871
C218	0.84373	0.59693	0.48381
C219	0.83416	0.56075	0.48343

N220	0.76916	0.54647	0.48562
C221	0.76194	0.51258	0.4866
N222	0.81932	0.49305	0.48487
C223	0.88334	0.5073	0.48189
N224	0.89108	0.54117	0.48135
C225	0.69151	0.49756	0.48902
C226	0.9448	0.48446	0.48093
C227	0.6973	0.46041	0.50244
C228	0.00795	0.49625	0.47625
C229	0.70469	0.14878	0.52408
C230	0.01541	0.18463	0.49794
C231	0.39262	0.75086	0.61363
C232	0.3198	0.89436	0.38637
O233	0.43965	0.76301	0.60306
O234	0.27274	0.88222	0.39693
C235	0.28383	0.36069	0.49625
C236	0.3557	0.34039	0.50003
C237	0.42545	0.35617	0.50259
C238	0.42377	0.39185	0.50163
C239	0.35279	0.4116	0.49756
C240	0.28172	0.39739	0.49413
C241	0.21499	0.34439	0.49283
C242	0.21769	0.30902	0.49455
C243	0.2873	0.28885	0.49781
C244	0.35705	0.30463	0.50038
C245	0.49506	0.336	0.50585
C246	0.49776	0.30063	0.50757
C247	0.42891	0.28433	0.50416
C248	0.43102	0.24763	0.50627
C249	0.35994	0.23342	0.50283
C250	0.28897	0.25317	0.49878
C251	0.20782	0.42249	0.48807
C252	0.49313	0.41062	0.50288
C253	0.50491	0.22253	0.51232
C254	0.21961	0.2344	0.49752
C255	0.18524	0.46182	0.46725
C256	0.11999	0.48564	0.46333
C257	0.07436	0.47065	0.47942
C258	0.09685	0.43154	0.50016
C259	0.16317	0.40818	0.50463
C260	0.57327	0.39456	0.53056
C261	0.63942	0.41125	0.53045
C262	0.62563	0.44486	0.50314

C263	0.54462	0.46173	0.47595
C264	0.4789	0.4447	0.47586
C265	0.52746	0.1832	0.53312
C266	0.59268	0.15938	0.53702
C267	0.63831	0.17438	0.52093
C268	0.61585	0.2135	0.50021
C269	0.54956	0.23685	0.49576
C270	0.13946	0.25047	0.46984
C271	0.0733	0.23379	0.46994
C272	0.08708	0.20017	0.49725
C273	0.16809	0.1833	0.52444
C274	0.23383	0.20032	0.52454
H275	0.07106	0.8702	0.54912
H276	0.76919	0.91688	0.47918
H277	0.65919	0.89088	0.45596
H278	0.05322	0.75432	0.54409
H279	0.94322	0.72831	0.52088
H280	0.64136	0.77499	0.45095
H281	0.0266	0.93247	0.50316
H282	0.02026	0.99393	0.50133
H283	0.8167	0.98124	0.52317
H284	0.82722	0.91912	0.52671
H285	0.12337	0.75886	0.5995
H286	0.27436	0.72861	0.63049
H287	0.30704	0.81456	0.55423
H288	0.15662	0.84461	0.52356
H289	0.68587	0.71271	0.49697
H290	0.69227	0.65122	0.49886
H291	0.8957	0.66391	0.47694
H292	0.88513	0.72606	0.47334
H293	0.58909	0.88634	0.40055
H294	0.4381	0.91659	0.36953
H295	0.40532	0.83066	0.44578
H296	0.55574	0.8006	0.47647
H297	0.96759	0.04299	0.50722
H298	0.8193	0.03684	0.52024
H299	0.77543	0.18852	0.5159
H300	0.07806	0.12771	0.5201
H301	0.74498	0.60212	0.49302
H302	0.89316	0.60828	0.47994
H303	0.63461	0.51733	0.48026
H304	0.93726	0.45651	0.48447
H305	0.75681	0.44066	0.51388

H306	0.01188	0.52515	0.47037
H307	0.70073	0.1199	0.52994
H308	0.9559	0.20438	0.48651
H309	0.41825	0.72617	0.63736
H310	0.29419	0.91905	0.36264
H311	0.35339	0.43879	0.49711
H312	0.15518	0.35946	0.48626
H313	0.16288	0.29827	0.49234
H314	0.54988	0.34675	0.50807
H315	0.55758	0.28555	0.51416
H316	0.35934	0.20624	0.50328
H317	0.21782	0.47422	0.45382
H318	0.10457	0.51576	0.44745
H319	0.06624	0.4189	0.51434
H320	0.18019	0.3787	0.52146
H321	0.58509	0.36848	0.55174
H322	0.70151	0.39786	0.55162
H323	0.53279	0.48728	0.45433
H324	0.41729	0.45758	0.45438
H325	0.49488	0.17079	0.54654
H326	0.60808	0.12926	0.55288
H327	0.64647	0.22614	0.48604
H328	0.53256	0.26634	0.47894
H329	0.12766	0.27655	0.44866
H330	0.01122	0.24719	0.44877
H331	0.17991	0.15774	0.54605
H332	0.29543	0.18743	0.54601
C333	0.20418	0.20015	0.83747
C334	0.22254	0.16334	0.84114
C335	0.30679	0.14154	0.85978
C336	0.3723	0.15667	0.87438
C337	0.3533	0.19264	0.87073
C338	0.27094	0.21506	0.85224
C339	0.12012	0.2213	0.8181
C340	0.05574	0.20651	0.80364
C341	0.07241	0.17032	0.80694
C342	0.15667	0.14853	0.82559
C343	0.32347	0.10536	0.86308
C344	0.25909	0.09057	0.84863
C345	0.17503	0.11171	0.82926
C346	0.10827	0.09681	0.81449
C347	0.0259	0.11922	0.796
C348	0.00691	0.1552	0.79234

C349	0.26016	0.25418	0.84825
C350	0.46227	0.13689	0.89241
C351	0.11905	0.05767	0.81851
C352	0.91694	0.17499	0.7743
C353	0.31425	0.27609	0.84112
C354	0.31024	0.31143	0.83987
C355	0.25142	0.32625	0.84527
C356	0.19606	0.30473	0.85185
C357	0.20171	0.26886	0.85388
C358	0.4965	0.1042	0.92274
C359	0.58247	0.08708	0.94037
C360	0.63543	0.1025	0.92797
C361	0.60104	0.13532	0.89763
C362	0.51522	0.15243	0.88008
C363	0.06501	0.03576	0.82567
C364	0.06905	0.0004	0.82696
C365	0.12785	0.98557	0.82155
C366	0.18316	0.0071	0.81494
C367	0.17747	0.04298	0.81287
C368	0.88274	0.20768	0.74397
C369	0.79676	0.2248	0.72632
C370	0.74378	0.20939	0.73871
C371	0.77814	0.17657	0.76905
C372	0.86396	0.15945	0.78662
C373	0.25323	0.36339	0.84482
C374	0.20218	0.38152	0.84973
C375	0.21181	0.41767	0.85017
N376	0.27685	0.43193	0.84801
C377	0.28412	0.4658	0.84707
N378	0.22675	0.48532	0.84882
C379	0.16269	0.47108	0.85176
N380	0.1549	0.43723	0.85226
C381	0.10126	0.49391	0.85274
C382	0.35458	0.48082	0.84467
C383	0.12609	0.94841	0.82205
C384	0.17713	0.93027	0.81714
C385	0.16756	0.89409	0.81676
N386	0.10256	0.87981	0.81895
C387	0.09534	0.84592	0.81994
N388	0.15272	0.82638	0.8182
C389	0.21674	0.84064	0.81523
N390	0.22448	0.87451	0.81468
C391	0.02491	0.83089	0.82235

C392	0.2782	0.81779	0.81426
C393	0.0307	0.79375	0.83577
C394	0.34135	0.82959	0.80958
C395	0.03809	0.48212	0.85742
C396	0.34881	0.51796	0.83127
C397	0.72602	0.0842	0.94697
C398	0.6532	0.2277	0.7197
O399	0.77305	0.09634	0.93639
O400	0.60614	0.21556	0.73027
C401	0.61723	0.69403	0.82958
C402	0.6891	0.67373	0.83336
C403	0.75885	0.68951	0.83593
C404	0.75717	0.72519	0.83496
C405	0.68619	0.74494	0.8309
C406	0.61512	0.73073	0.82746
C407	0.54839	0.67773	0.82617
C408	0.55109	0.64235	0.82789
C409	0.6207	0.62218	0.83114
C410	0.69045	0.63796	0.83371
C411	0.82846	0.66934	0.83919
C412	0.83116	0.63396	0.84091
C413	0.76231	0.61766	0.83749
C414	0.76442	0.58097	0.8396
C415	0.69334	0.56676	0.83617
C416	0.62237	0.58651	0.83211
C417	0.54122	0.75583	0.8214
C418	0.82653	0.74396	0.83622
C419	0.83831	0.55587	0.84565
C420	0.55301	0.56774	0.83085
C421	0.51864	0.79516	0.80058
C422	0.45339	0.81898	0.79666
C423	0.40776	0.80399	0.81276
C424	0.43025	0.76487	0.8335
C425	0.49657	0.74152	0.83796
C426	0.90667	0.7279	0.86389
C427	0.97282	0.74459	0.86379
C428	0.95903	0.7782	0.83647
C429	0.87802	0.79506	0.80928
C430	0.8123	0.77803	0.80919
C431	0.86086	0.51654	0.86645
C432	0.92608	0.49272	0.87035
C433	0.97171	0.50771	0.85426
C434	0.94925	0.54684	0.83354

C435	0.88296	0.57019	0.82909
C436	0.47286	0.58381	0.80317
C437	0.4067	0.56712	0.80327
C438	0.42048	0.53351	0.83058
C439	0.50149	0.51663	0.85777
C440	0.56723	0.53366	0.85787
H441	0.40446	0.20353	0.88245
H442	0.10259	0.25022	0.81251
H443	0.99259	0.22421	0.78929
H444	0.38662	0.08766	0.87742
H445	0.27662	0.06165	0.85421
H446	0.97476	0.10833	0.78428
H447	0.36	0.26581	0.83649
H448	0.35366	0.32727	0.83466
H449	0.1501	0.31457	0.8565
H450	0.16062	0.25246	0.86005
H451	0.45677	0.0922	0.93284
H452	0.60776	0.06195	0.96383
H453	0.64044	0.1479	0.88756
H454	0.49002	0.17795	0.8569
H455	0.01927	0.04605	0.8303
H456	0.02567	0.98456	0.8322
H457	0.2291	0.99725	0.81028
H458	0.21853	0.05939	0.80667
H459	0.92249	0.21967	0.73388
H460	0.7715	0.24993	0.70287
H461	0.73872	0.164	0.77911
H462	0.88914	0.13394	0.8098
H463	0.30099	0.37633	0.84055
H464	0.1527	0.37018	0.85357
H465	0.10883	0.52185	0.84923
H466	0.41146	0.46105	0.85343
H467	0.07838	0.93546	0.82635
H468	0.22656	0.94161	0.81327
H469	0.96801	0.85067	0.81359
H470	0.27066	0.78984	0.8178
H471	0.09021	0.77399	0.84721
H472	0.34528	0.85848	0.8037
H473	0.03413	0.45323	0.86327
H474	0.2893	0.53772	0.81984
H475	0.75165	0.05951	0.9707
H476	0.62759	0.25238	0.69597
H477	0.68679	0.77213	0.83045

H478	0.48858	0.6928	0.81959
H479	0.49628	0.6316	0.82567
H480	0.88328	0.68008	0.84141
H481	0.89098	0.61889	0.84749
H482	0.69274	0.53957	0.83661
H483	0.55122	0.80755	0.78716
H484	0.43797	0.8491	0.78078
H485	0.39964	0.75224	0.84767
H486	0.51359	0.71204	0.8548
H487	0.91849	0.70182	0.88508
H488	0.03491	0.73119	0.88495
H489	0.86619	0.82061	0.78766
H490	0.75069	0.79092	0.78772
H491	0.82828	0.50413	0.87987
H492	0.94148	0.4626	0.88622
H493	0.97987	0.55948	0.81937
H494	0.86596	0.59967	0.81227
H495	0.46106	0.60989	0.78199
H496	0.34462	0.58052	0.78211
H497	0.51331	0.49108	0.87939
H498	0.62883	0.52077	0.87934

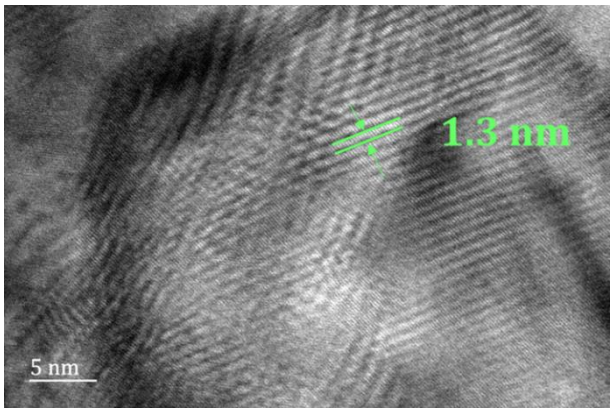

Figure S3. HR-TEM image of PTO-COF.

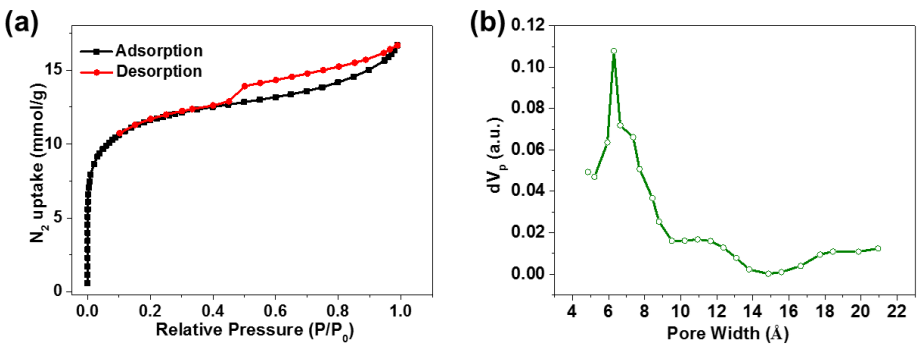

Figure S4. Nitrogen adsorption experiment of PTO-COF. (a) N_2 adsorption isotherm of PTO-COF. (b) PSD of PTO-COF from NLDFT model.

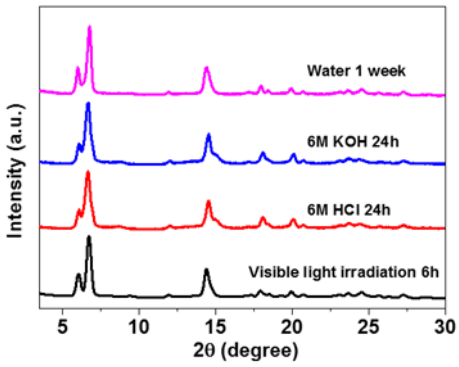

Figure S5. Chemical stability test of PTO-COF.

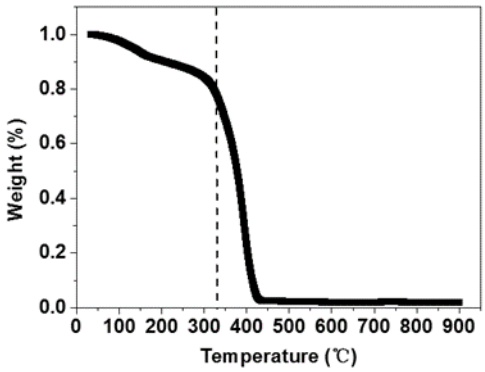

Figure S6. Thermogravimetric test of PTO-COF.

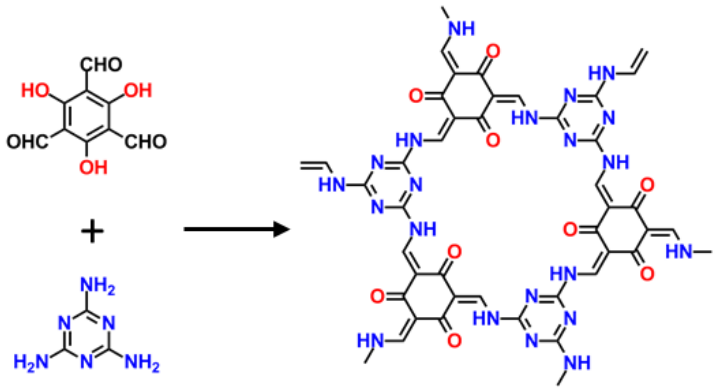

Figure S7. Schematic diagram of synthesis of TpMa-COF.

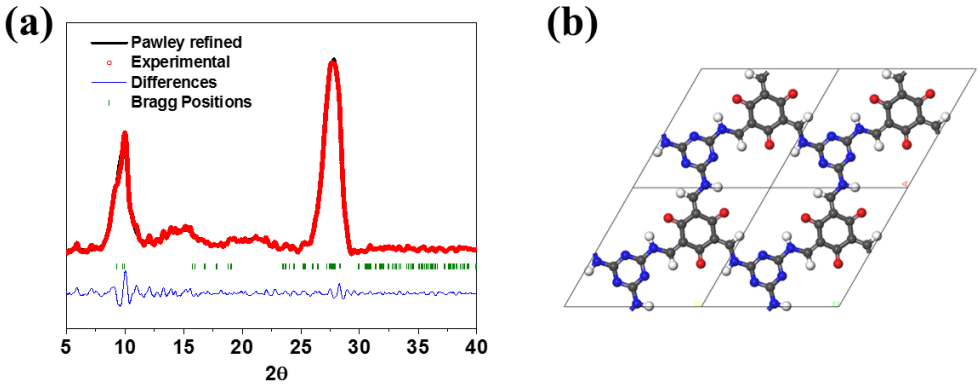

Figure S8. (a) Comparison of the experimental PXRD pattern of TpMa-COF (red pots) with the Pawley refined pattern (black), difference plot (blue) and Bragg positions (green). (b) AA stacking model of TpMa-COF.

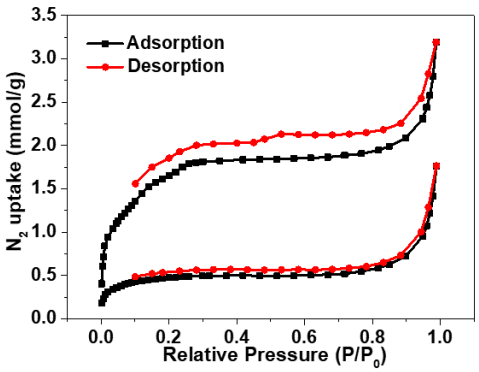

Figure S9. N_2 adsorption isotherm of TpMa-COF (up) and TpMa-CON (down).

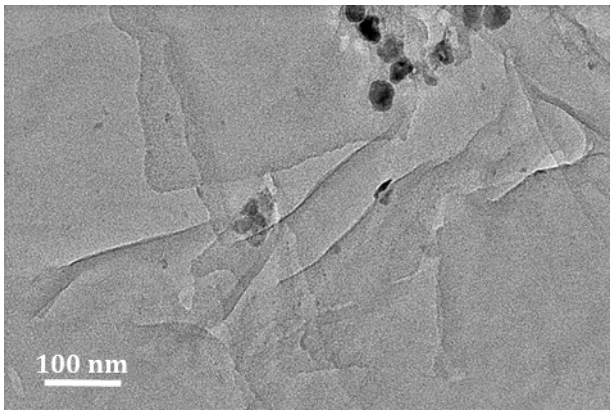

Figure S10. TEM image of TpMa-CON.

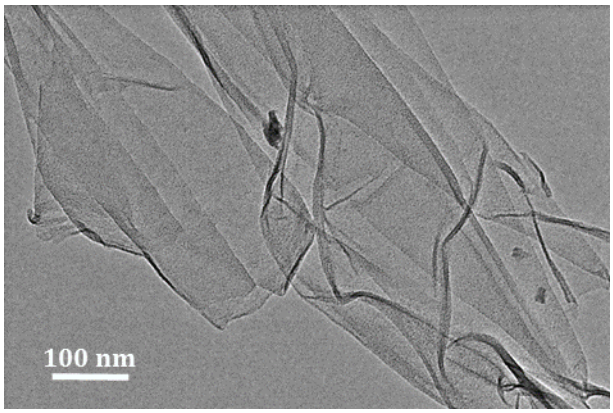

Figure S11. TEM image of PTO-CON.

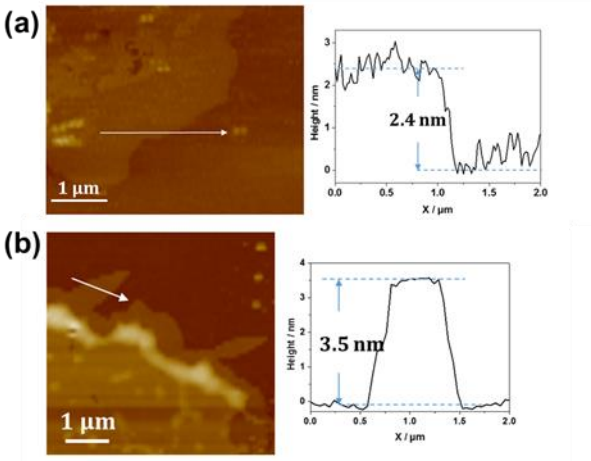

Figure S12. AFM images of TpMa-CON (a) and PTO-CON (b).

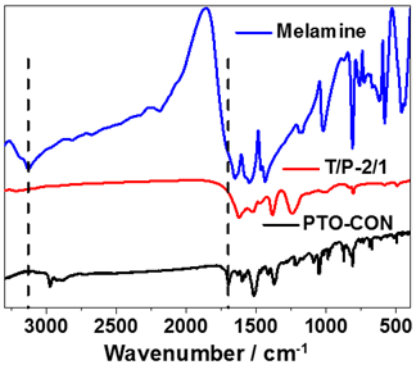

Figure S13. The comparison of FT-IR spectra of melamine, PTO-CON and T/P-2/1.

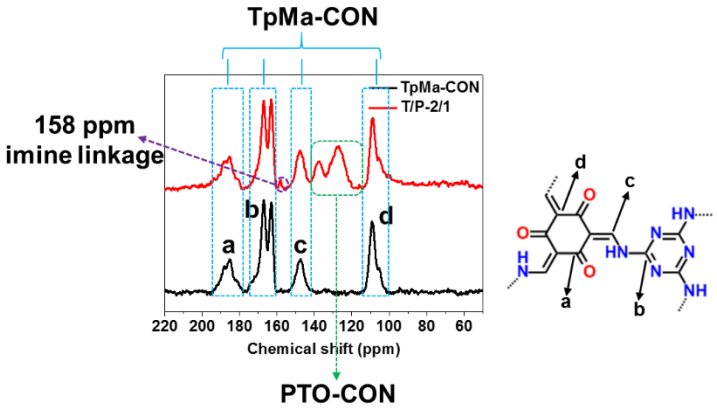

Figure S14. NMR spectrum of TpMa-CON (black) and T/P-2/1 (red).

Actually, the splitting of b signal in solid-state ^{13}C CP-MAS NMR assigned to the triazine carbon was also observed in that of TpMa-COF synthesized by solvothermal method.[1] Relevant report[2] indicated that the ^{13}C CP-MAS NMR spectrum of melamine also showed peak splitting, while only one peak was observed in the ^{13}C NMR spectrum of melamine dissolved in DMSO, which may be due to the fact that the cross-polarization experiments were not reliable enough to obtain fine quantitative signal intensity distribution.

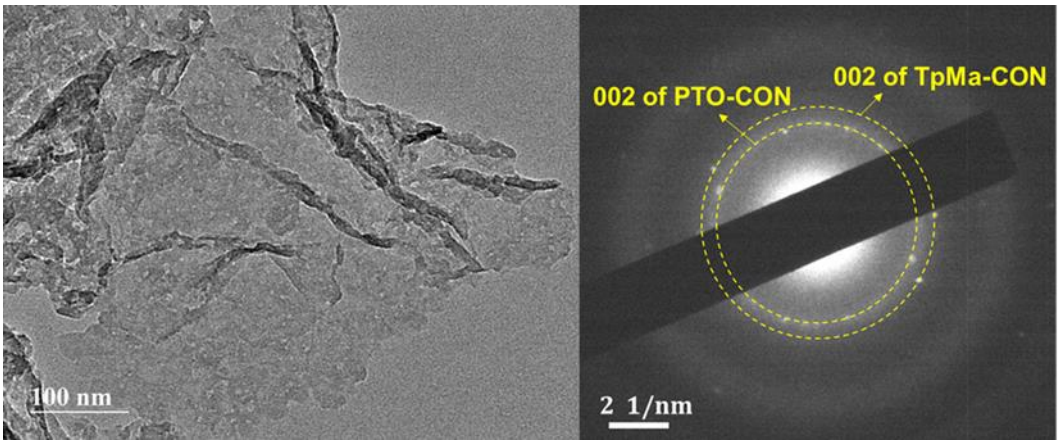

Figure S15. TEM and SAED image of T/P-2/1.

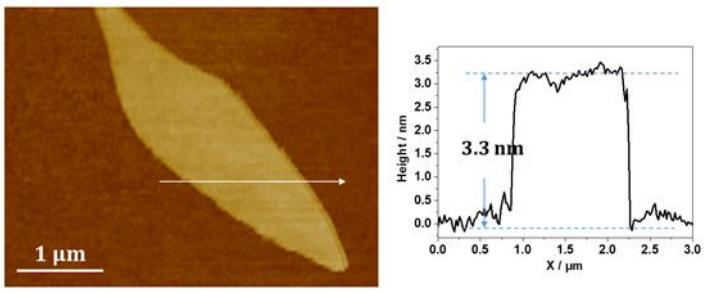

Figure S16. AFM images and thickness of T/P-2/1.

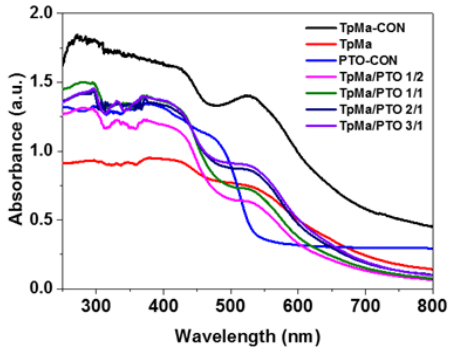

Figure S17. UV-DRS patterns of PTO-CON, TpMa-CON, T/P-1/2, 1/1, 2/1,3/1.

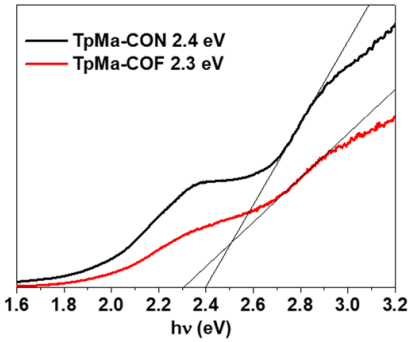

Figure S18. Tauc plots of TpMa-CON and TpMa-COF.

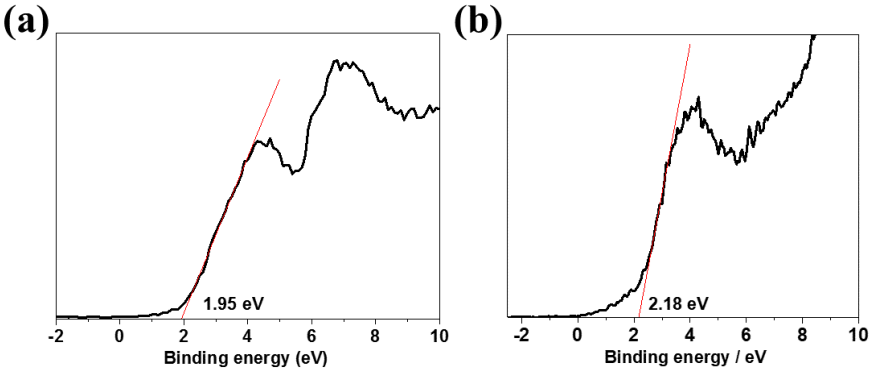

Figure S19. VB XPS spectrum of TpMa-COF (a) and TpMa-CON (b).

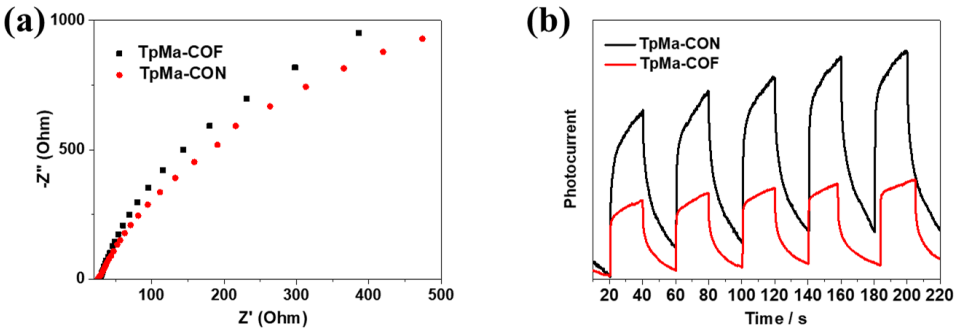

Figure S20. EIS Nyquist plots (a) and photocurrents (b) of TpMa-COF/CON.

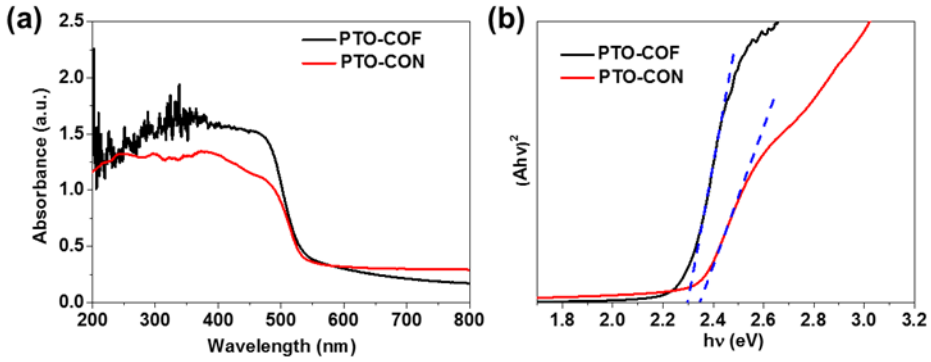

Figure S21. UV-DRS patterns (a) and Tauc plots (b) of PTO-COF and PTO-CON.

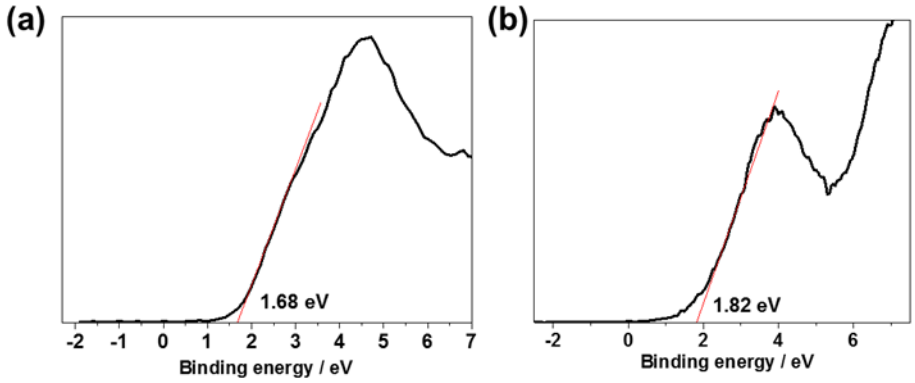

Figure S22. VB XPS spectra of PTO-COF (a) and PTO-CON (b).

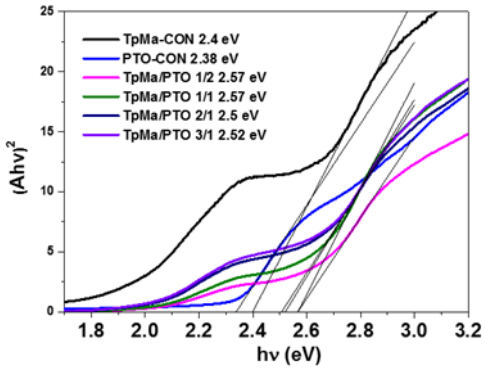

Figure S23. Tauc plots of PTO-CON, TpMa-CON, T/P-1/2, 1/1, 2/1,3/1.

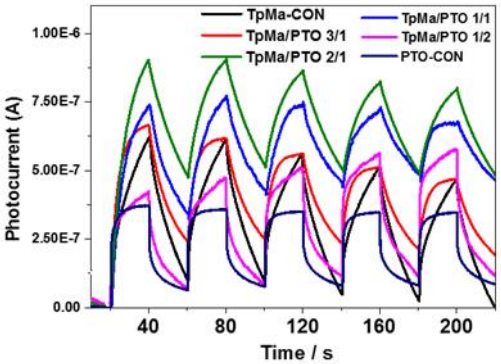

Figure S24. Photocurrents tests of PTO-CON, TpMa-CON, T/P-1/2, 1/1, 2/1,3/1.

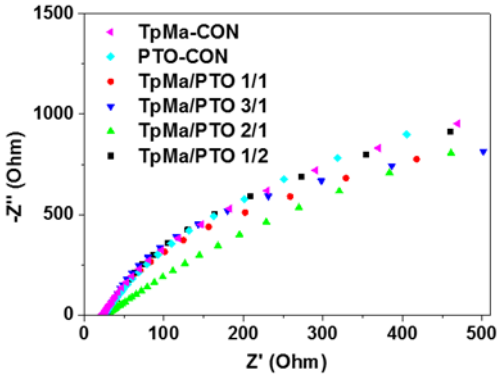

Figure S25. EIS Nyquist plots of PTO-CON, TpMa-CON, T/P-1/2, 1/1, 2/1,3/1.

Section S3 Photocatalytic degradation of antibiotics by PTO-COF

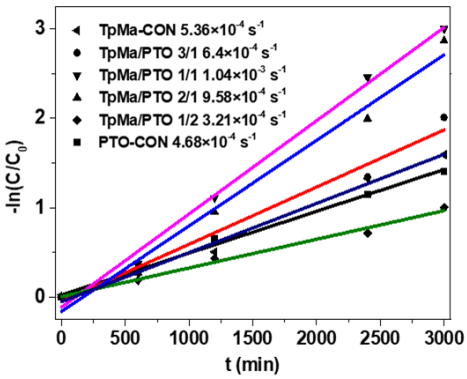

Figure S26. Kinetics linear simulation curves of sulfamethazine photocatalytic degradation by PTO-CON, TpMa-CON, T/P-1/2, 1/1, 2/1,3/1.

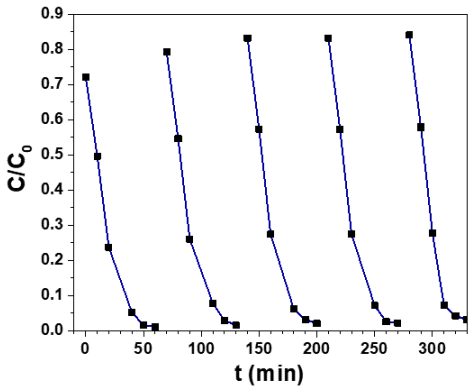

Figure S27. Reusability of T/P-2/1 heterojunction for the photodegradation of 10 ppm sulfamethazine.

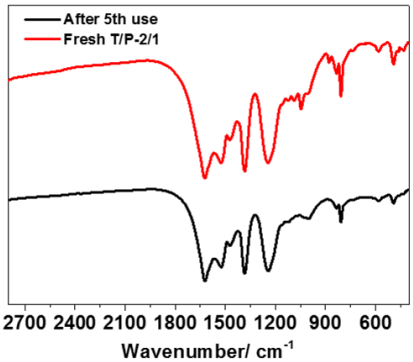

Figure S28. FT-IR spectrum of T/P-2/1 and after 5th use of it for photocatalytic degradation.

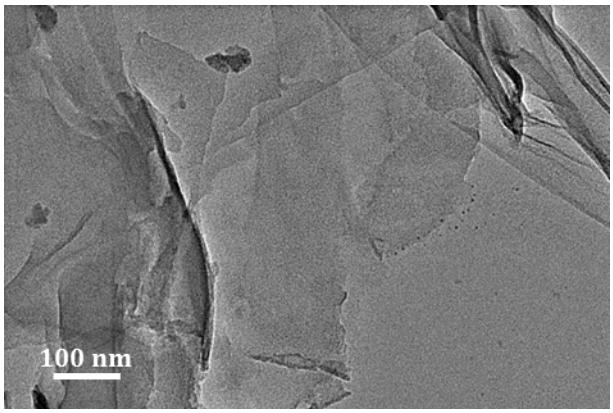

Figure S29. TEM image of T/P-2/1 after 5th use in photocatalytic degradation.

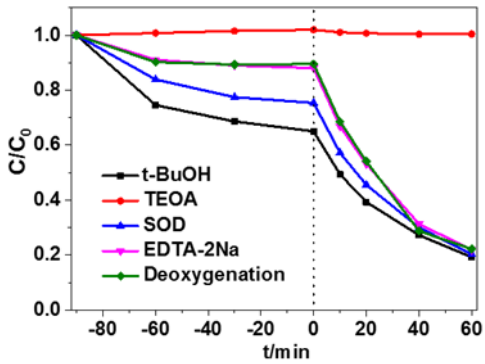

Figure S30. Trapping experiments of photocatalytic degradation for TpMa-CON.

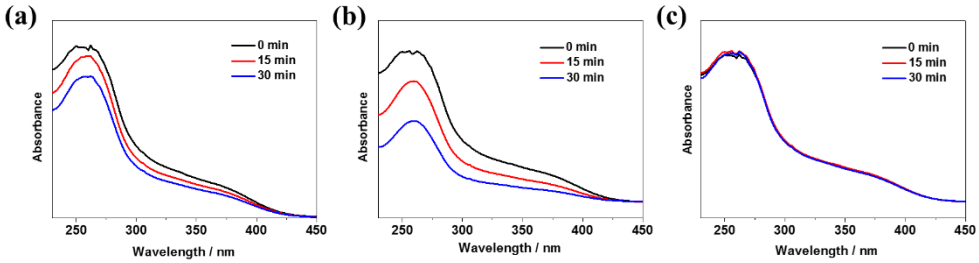

Figure S31. NBT reduction experiment by PTO-CON (a), T/P-2/1 (b), and TpMa-CON (c) under illumination.

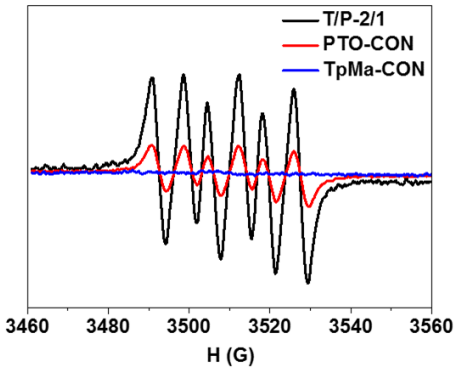

Figure S32. Detection of superoxide radicals by ESR. ESR spectrum of the solution of DMPO in 5 mL air-saturated MeOH upon irradiation for 20 min with T/P-2/1 (black), PTO-CON (red) and TpMa-CON (blue).

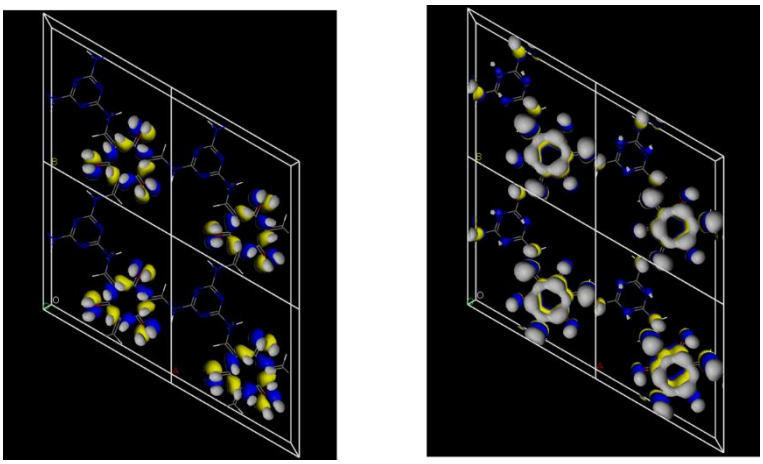

Figure S33. Locations of HOMO (left) and LUMO (right) in TpMa-CON.

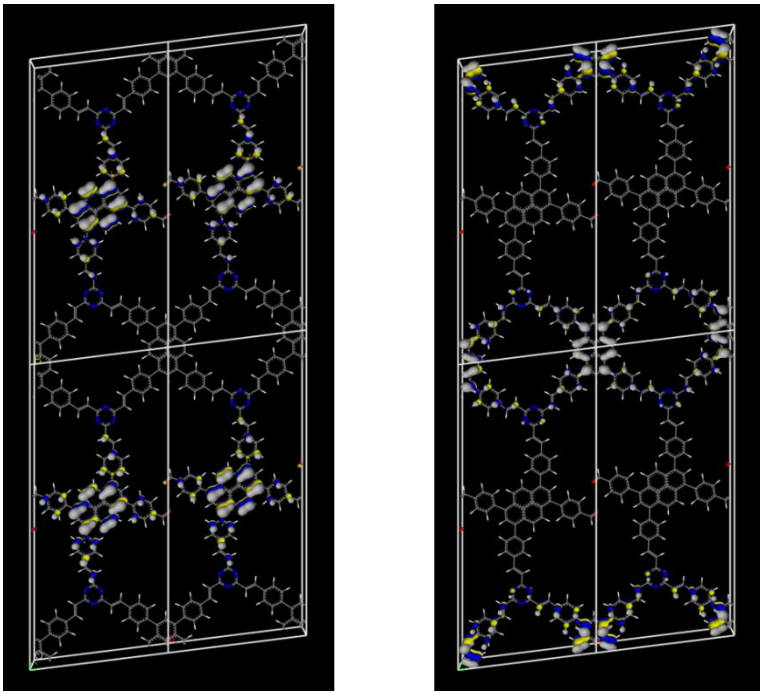

Figure S34. Locations of HOMO (left) and LUMO (right) in PTO-CON.

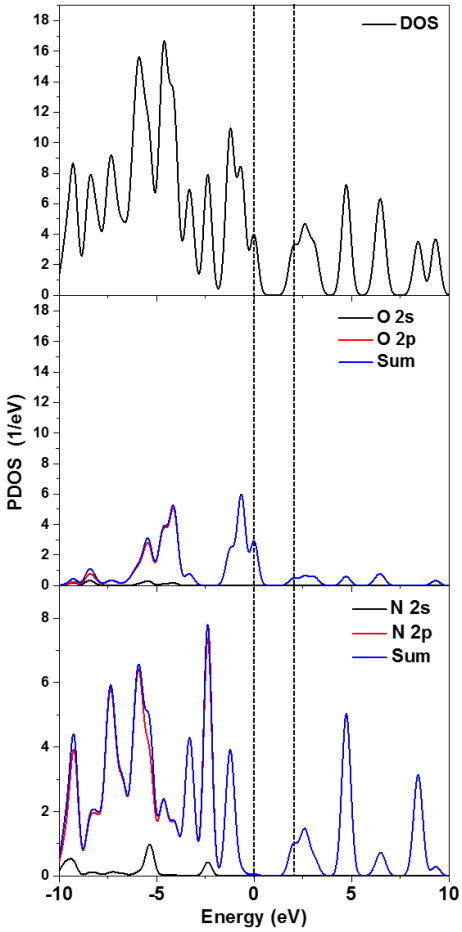

Figure S35. DOS and PDOS analysis for TpMa-CON.

References

1. Bhadra, M.; Kandambeth, S.; Sahoo, M. K.; Addicoat, M.; Balaraman, E.; Banerjee, R. Triazine Functionalized Porous Covalent Organic Framework for Photo-organocatalytic E-Z Isomerization of Olefins. *J. Am. Chem. Soc.* **2019**, *141* (15), 6152-6156.

2. Jürgens, B.; Irran, E.; Senker, J.; Kroll, P.; Müller, H.; Schnick, W. Melem (2,5,8-Triamino-tri-s-triazine), an Important Intermediate during Condensation of Melamine Rings to Graphitic Carbon Nitride: Synthesis, Structure Determination by X-ray Powder Diffractometry, Solid-State NMR, and Theoretical Studies. *J. Am. Chem. Soc.* **2003**, 125, 10288−10300