Electronic Supplementary Information

Post-Cyclization of a Bisimine-Linked Covalent Organic Framework to Enhance the Performance of Visible-Light Photocatalytic Hydrogen Evolution

Huanyu Liu,[a] Yueting Li,[a] Lu Dai,[a] Xiangjian Meng,[a] Anwang Dong,[a] Zimo Zhou,[a] Huixia Lv,[a] Pengfei Li,, [a] and Bo Wang [a, b]*

[a]Frontiers Science Center for High Energy Material, Key Laboratory of Cluster Science Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Advanced Research Institute of Multidisciplinary Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China

[b]Advanced Technology Research Institute (Jinan), Beijing Institute of Technology, Jinan, 250300, China

*E-mail: lipengfei@bit.edu.cn

Table of Contents

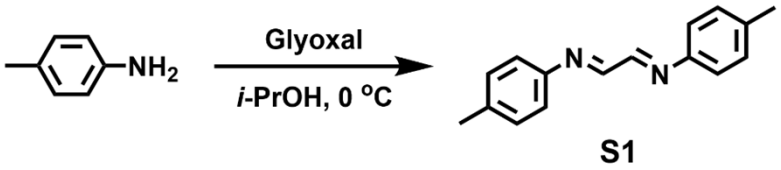
Section S1. *Reagents and Instruments*

Reagents: All chemicals were commercially available and used without further purification. The 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl) tetraaniline was purchased from Bide Pharmatech Ltd. H_2PtCl_6 was purchased from MACKLIN. Ascorbic acid was purchased from TCI. Glyoxal (40% aqueous solution), 1,4-dioxane, benzyl alcohol, mesitylene, tetrahydrofuran, chloromethyl ethyl ether, methanol, and acetone were purchased from Beijing Chemical Regent Company.

Instruments: Fourier transform infrared (FT-IR) spectra were collected in the range of 400–4000 cm^{-1} on Bruker ALPHA spectrometer. Powder X-ray diffraction (PXRD) analysis was carried out on a Rigaku MiniFlex 600 diffractometer operating at 40 kV voltage and 15 mA current with Cu-Kα X-ray radiation (λ = 0.154056 nm). Thermogravimetric analysis (TGA, Shimadzu DTG-60) was performed from room temperature to 800 ℃ at a heating rate of 10 ℃/min and a N_2 flow rate of 50 mL/min. The nitrogen physisorption experiment was conducted at 77 K on a Quantachrome Instrument Autosorb-iQ after pretreatment. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was evaluated by the non-local density functional theory (NLDFT). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded by a Bruker Advance III 400 MHz or 500 MHz NMR spectrometer. Solid-state ^{13}C CP/MAS NMR spectra were performed on a Bruker AVANCE III 700 MHz NMR spectrometer. Scanning electron microscopy (SEM) images were acquired from a JEOL model JSM-7500F scanning electron microscope. The samples were sputter-coated with platinum layers to increase their conductivity before observation. Transmission electron microscopy (TEM) images were collected on JEOL JEM-2100 transmission electron microscopes operating at 200 kV. Electrochemical tests were carried out on a CHI760E electrochemical workstation. UV/Visible diffuse-reflectance (UV/Vis DRS) spectra were collected on a Shimadzu

Corporation UV-2600 spectrometer. Photoluminescence and time-resolved PL decay spectra were collected on a Horiba FluoroLog-3 under air. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL JES-FA200 spectrometer. The content of platinum was measured by inductively coupled plasma-mass spectrometry (ICP-MS).

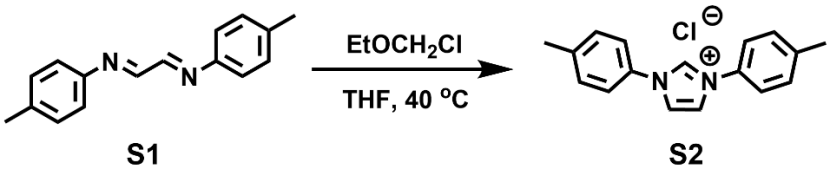
Section S2. *Synthetic procedures and measurements*



Scheme S1. The synthesis of model compound S1.

Model Compound S1

Glyoxal (0.636 mL, 5 mmol, 1.0 eq.) was added to a stirred solution of 4-methylaniline (1.07 g, 10.0 mmol, 2.0 eq.) in isopropyl alcohol at 0 ℃. The resulting solution was stirred for 4 h. The precipitate was filtered, washed with isopropyl alcohol and dried under vacuum to give a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H), 7.26 (br. s, 8H), 2.39 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 (s), 147.6 (s), 138.2 (s), 130.1(s), 121.4(s), 21.2(s). The ^{1}H NMR and ^{13}C NMR spectra of model compound S1 are consistent with previously reported.[1]



Scheme S2. The synthesis of model compound S2.

Model Compound S2

A solution of chloromethyl ethyl ether (574 μL, 6 mmol, 1.5 eq.) was added dropwise to a stirred solution of the model compound S1 (946 mg, 4 mmol, 1.0 eq.) in EtOAc at room temperature under N_2. The resulting solution was stirred for 16 h. The precipitate was filtered, washed with EtOAc (20 mL) and dried under vacuum to give the model compound S2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 7.96 (d, J = 8.0 Hz, 4H), 7.72 (s, 2H), 7.41 (d, J = 8.0 Hz, 4H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 140.9 (s), 132.6 (s), 130.6 (s), 130.3(s), 122.2(s), 19.7(s).

The ^{1}H NMR and ^{13}C NMR spectra of model compound S2 are consistent with previously reported.[1]

PyG-COF

PyTTA (22.6 mg, 0.4 mmol, 1.0 eq.) and glyoxal (10.1 μL, 0.8 mmol, 2.0 eq.) were mixed in a Schlenk tube. After that, mesitylene (1 mL), benzyl alcohol (1 mL) and 6 M acetic acid (HOAc) (0.2 mL) were added. The resultant mixture was ultrasonicated for 5 min, and then degassed through three freeze-pump-thaw cycles and sealed under vacuum. The suspension was heated at 120 °C and left undisturbed for 3 days. The orange solid was isolated by filtration and washed with anhydrous tetrahydrofuran and acetone.

PyG-Im-COF

An oven-dried flask was charged with PyG-COF (30 mg), chloromethyl ethyl ether (10 μL), and anhydrous tetrahydrofuran (15 mL) under N_2. The flask was heated at 40 ℃ and stirred for 2 days. The resultant solid was isolated by filtration and washed with anhydrous ethyl acetate, and then dried under vacuum to afford a yellow solid.

Photoelectrochemical measurement

To fabricate the working electrode, 5 mg of COF, 1 mL of ethanol, and 10 μL of 5% Nafion in water were mixed under sonication for 30 min to make the sample fully dispersed. The resultant slurry was dropped onto a piece of fluoride-tin oxide (FTO) glass substrate with a cover area of 0.25 cm^2. The uncovered parts of the electrode were coated with epoxy. The working electrode was dried in air naturally. The photocurrents were recorded by an electrochemical workstation equipped with a conventional three-electrode cell. A platinum plate electrode and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrodes were immersed in a 0.2 M aqueous Na_2SO_4 solution. The working electrode was

illuminated by a 300 W Xe lamp (PLS-SXE300C) with a 420 nm cut-off filter from the backside. Each measurement was repeated three times under ambient conditions.

Photocatalytic measurement

COFs (10 mg) were dispersed in 15 mL of 0.1 M ascorbic acid aqueous solution, sonicated for 15 min to obtain a uniformly dispersed suspension, and then 10 μL of 40 mg L^{-1} H_2PtCl_6 was added. The mixed suspension was transferred to a glass reactor of the Labsolar-6A photocatalytic equipment. After the whole reaction system was evacuated to remove the air in the system, a 300 W Xe lamp ($\lambda > 420$ nm) was used to irradiate the suspension. Circulating cooling water was used to keep the whole reaction system at 5 °C. Before the photocatalytic hydrogen production, H_2PtCl_6 was reduced for one hour to *in situ* form Pt nanoparticles. During the photocatalytic reaction, the generated gas product was analyzed by GC-2014C gas chromatography, which was sampling for every 30 min in 4 hours.

Determination of apparent quantum yield

The measurement of apparent quantum yield for photocatalytic hydrogen production of COFs is similar to the procedure in photocatalytic measurement under 300 W Xe lamp with different monochromatic filters (420, 450, 500, 520, and 550 nm). Using an optical power meter (Thorlabs PM100D), the optical power density at each wavelength was 10.2 mW cm^{-2}, and the light emission area was 19.6 cm^2. The AQY was calculated by using the following equation based on the amount of hydrogen produced in the photocatalytic reaction within one hour.

$$\eta_{AQY} = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where, M is the amount of H_2, N_A is the Avogadro constant (6.02×10^{23} mol^{-1}), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^8 m s^{-1}), S is the irradiation area (cm^2), P is the intensity of irradiation light (W cm^{-2}), t is the photoreaction time (s), λ is the wavelength of

the monochromatic light (nm).

Section S3. *Characterizations*

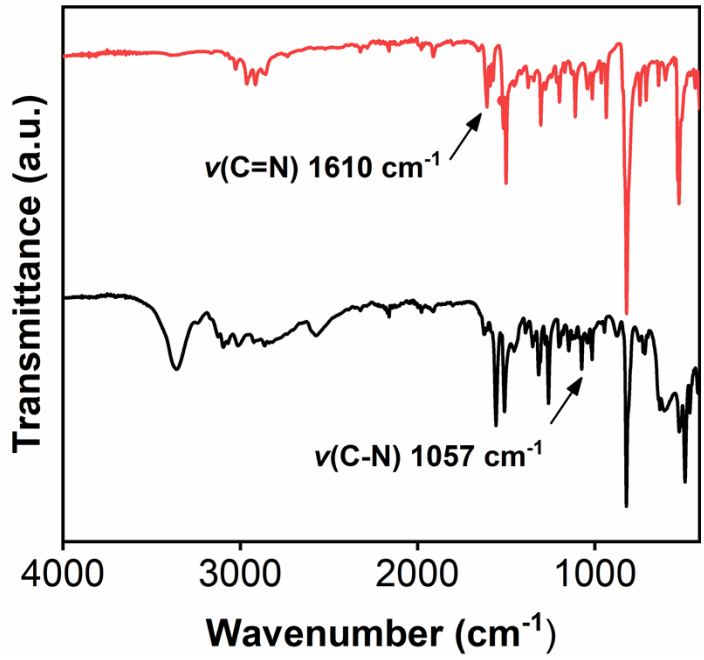


Figure S1. FT-IR spectra of model compound S1 (red) and model compound S2 (black).

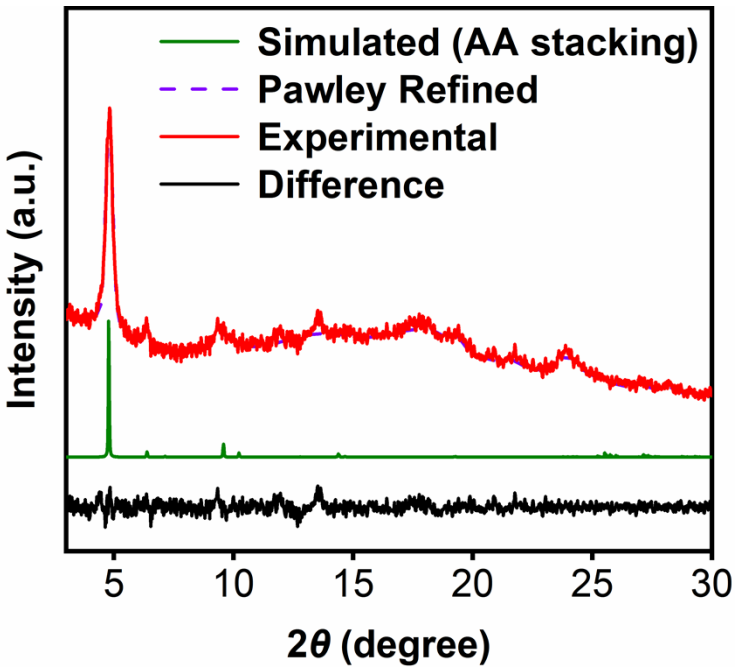


Figure S2. Comparison of experimental and simulated PXRD of PyG-COF.

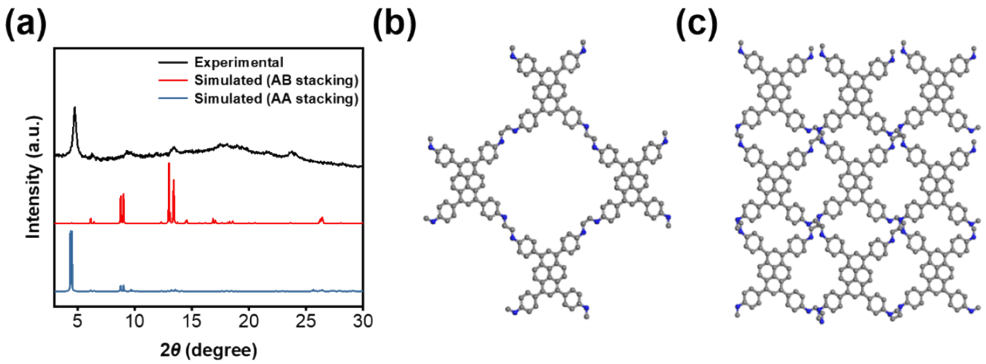


Figure S3. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 1. (b-c) The AA stacking and AB stacking of structural model 1.

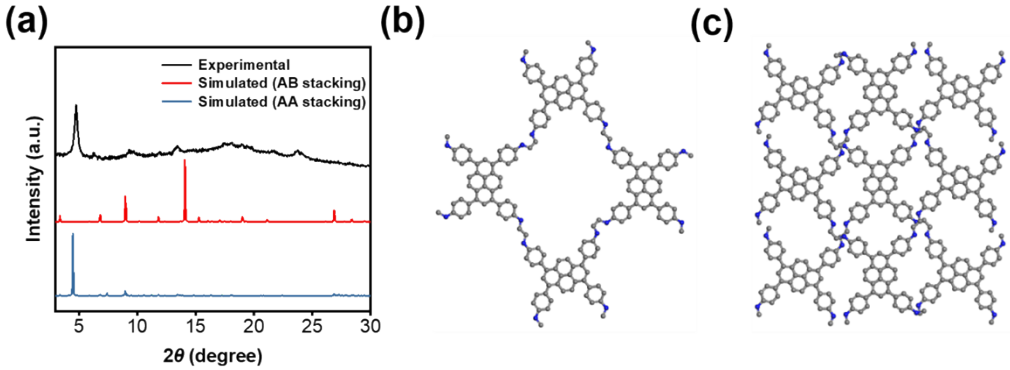


Figure S4. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 2. (b-c) The AA stacking and AB stacking of structural model 2.

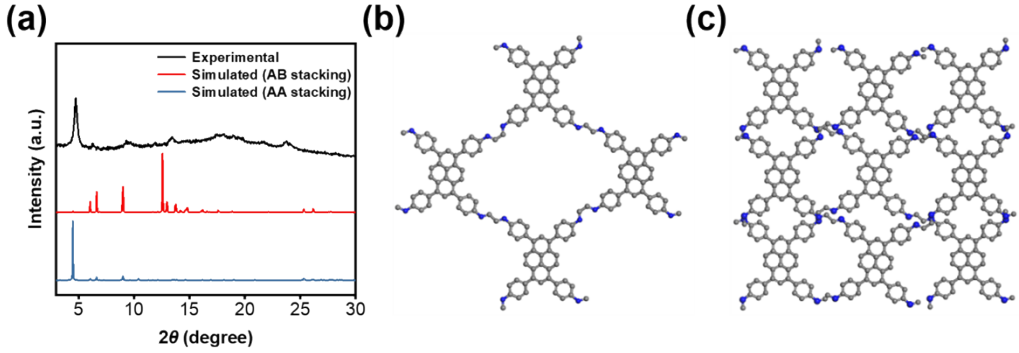


Figure S5. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 3. (b-c) The AA stacking and AB stacking of structural model 3.

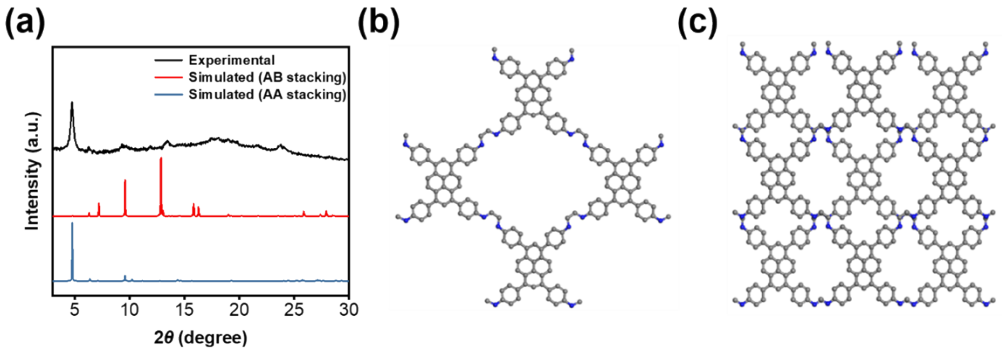


Figure S6. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 4. (b-c) The AA stacking and AB stacking of structural model 4.

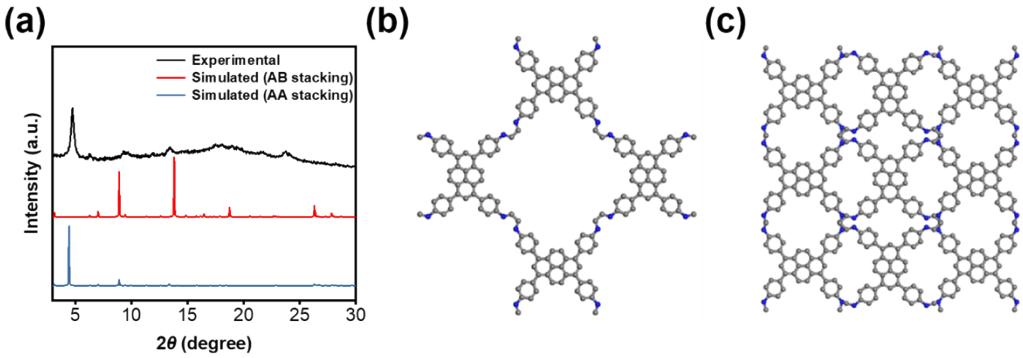


Figure S7. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 5. (b-c) The AA stacking and AB stacking of structural model 5.

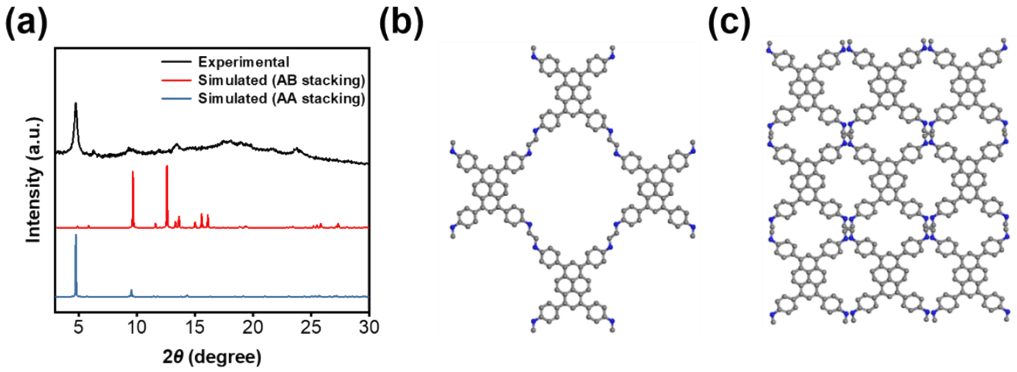


Figure S8. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 6. (b-c) The AA stacking and AB stacking of structural model 6.

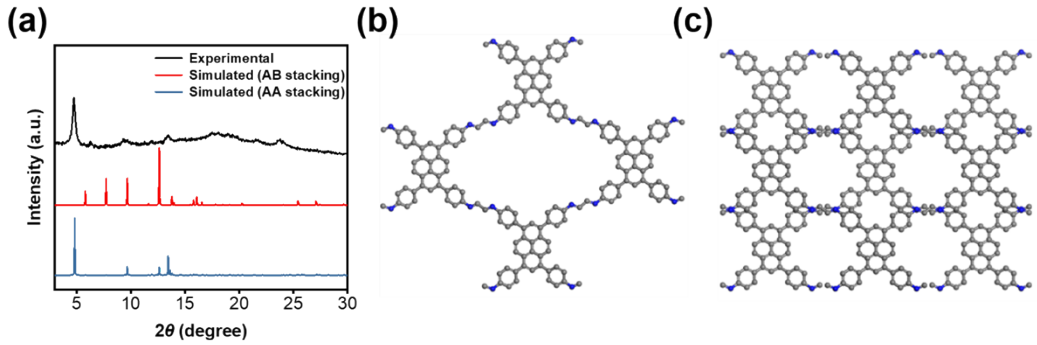


Figure S9. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 7. (b-c) The AA stacking and AB stacking of structural model 7.

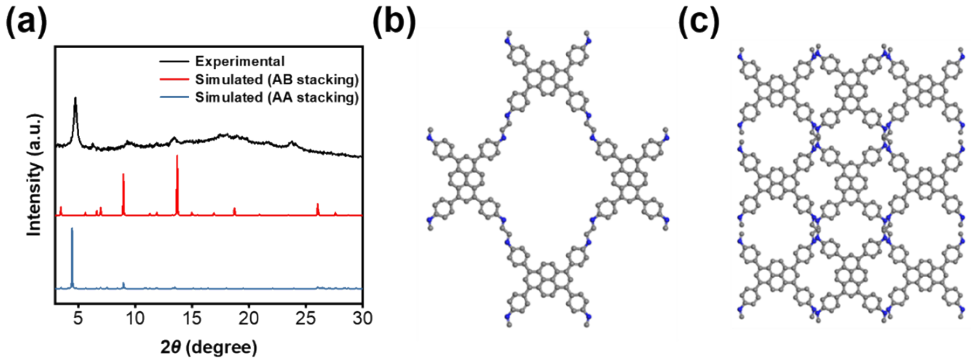


Figure S10. (a) The comparison of experimental and simulated PXRD patterns of PyG-COF in structural model 8. (b-c) The AA stacking and AB stacking of structural model 8.

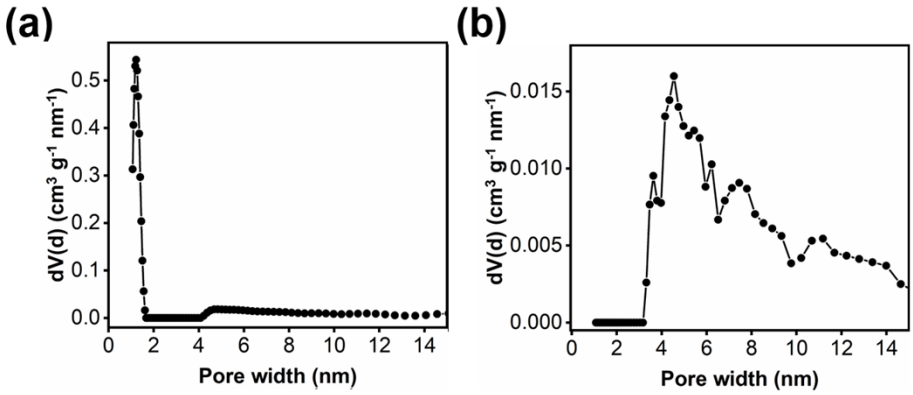


Figure S11. Pore size distributions for (a) PyG-COF and (b) PyG-Im-COF.

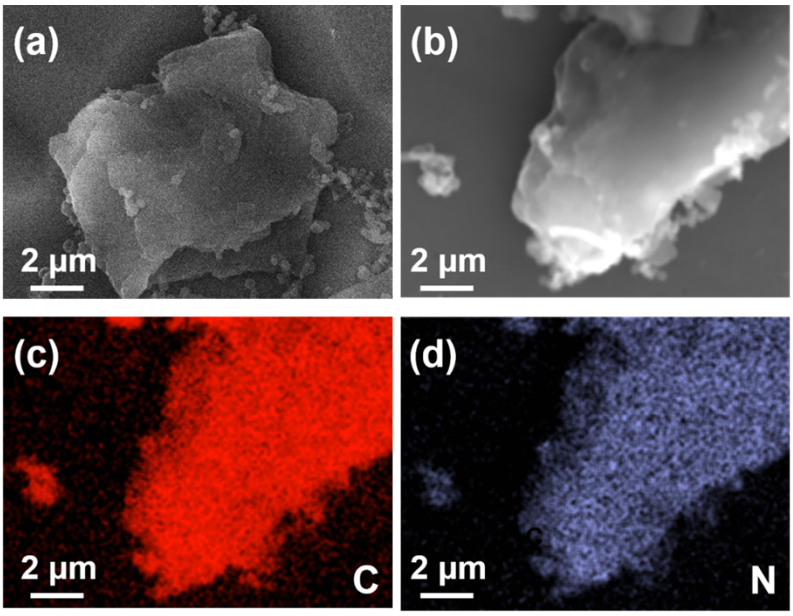


Figure S 12. SEM images of (a-b) PyG-COF and (c-d) EDS elemental mapping of PyG-COF.

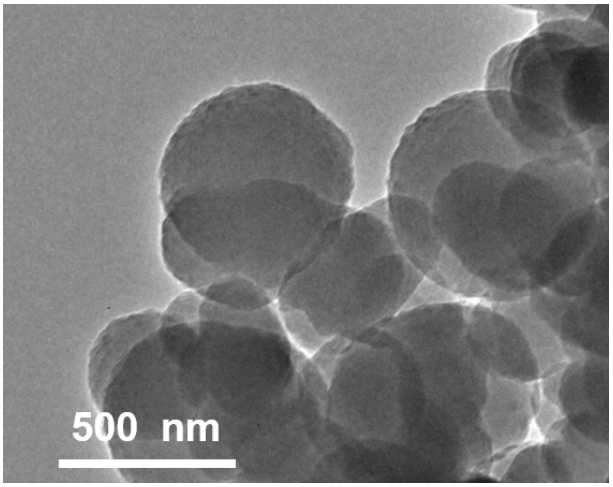


Figure S13. TEM image of PyG-COF.

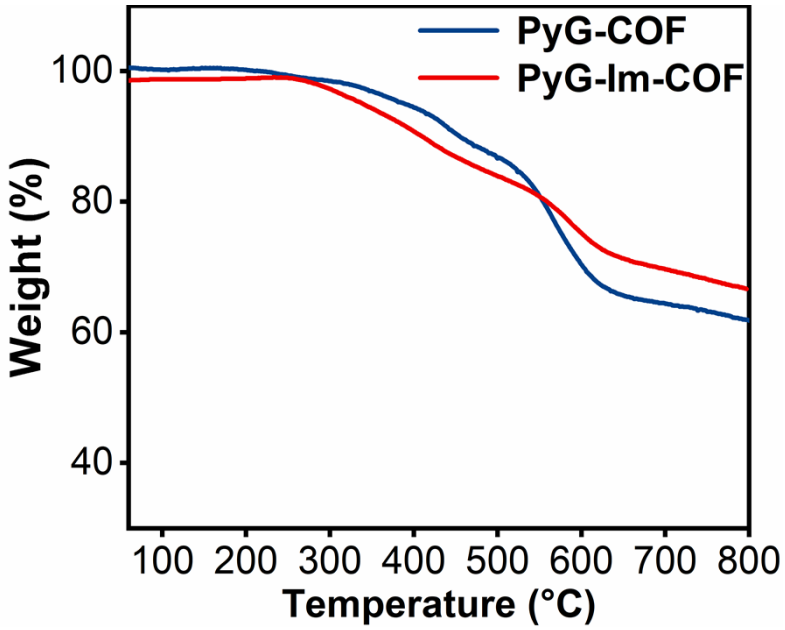


Figure S14. TGA curves of PyG-COF and PyG-Im-COF.

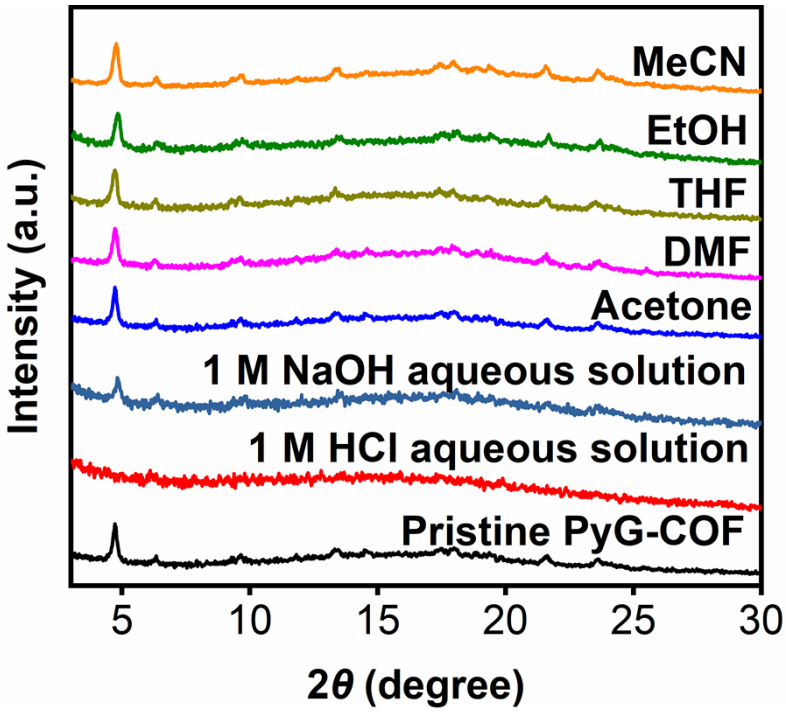


Figure S15. PXRD patterns of PyG-COF after treated upon different organic solvents for 2 days.

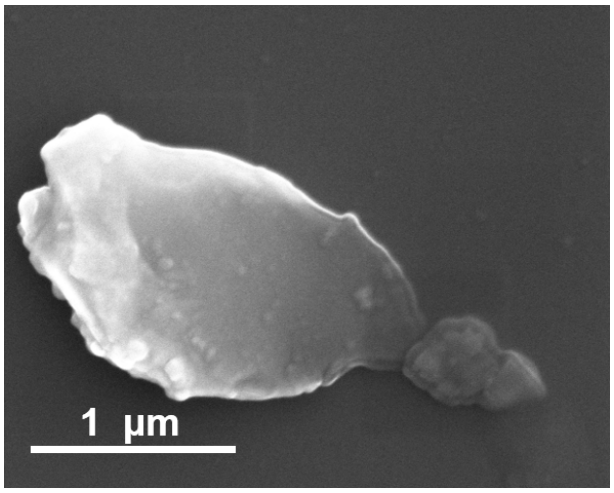


Figure S16. SEM image of PyG-Im-COF.

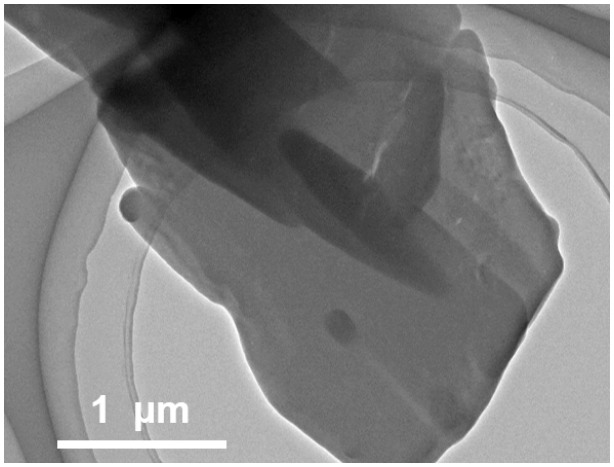


Figure S17. TEM image of PyG-Im-COF.

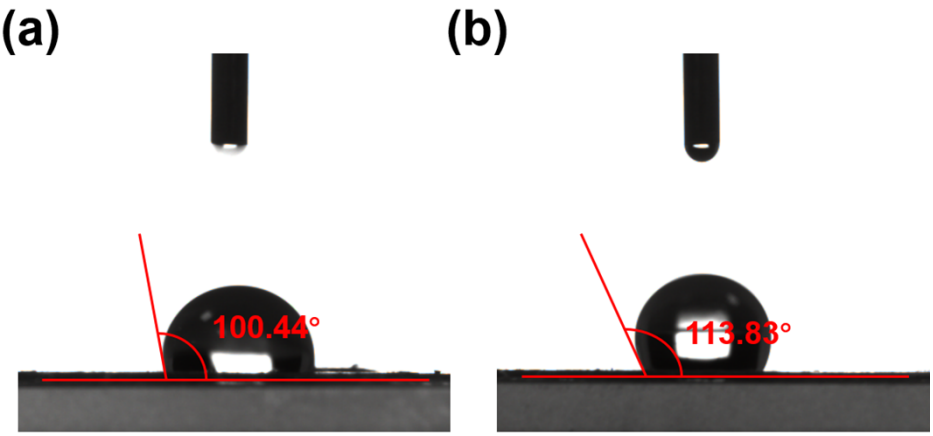


Figure S18. The water contact angle photos for (a) PyG-COF and (b) PyG-Im-COF.

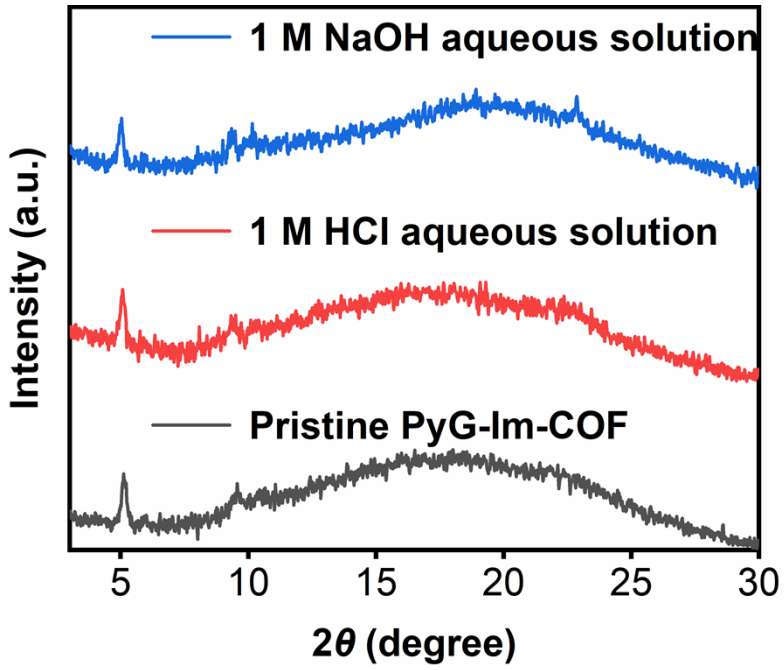


Figure S19. PXRD patterns of PyG-Im-COF after treated upon different conditions for 2 days.

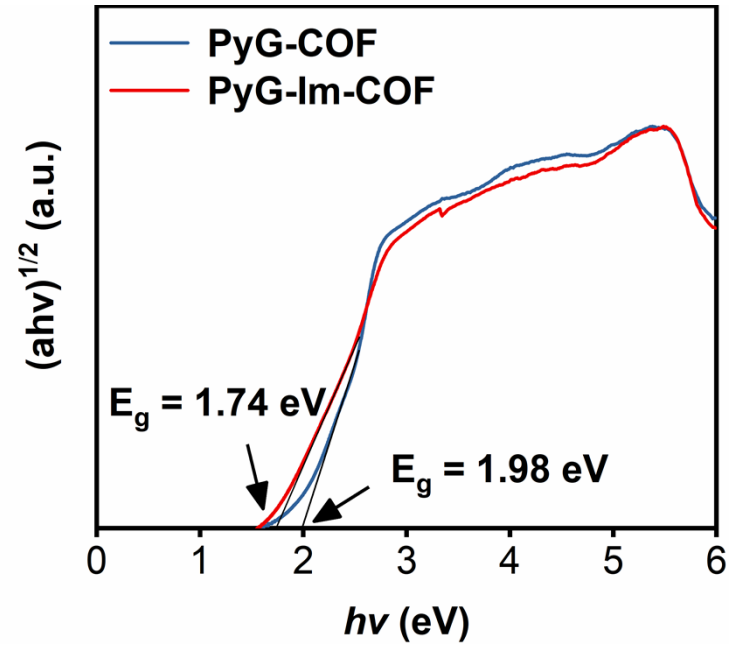


Figure S20. Tauc plots of the PyG-COF and PyG-Im-COF.

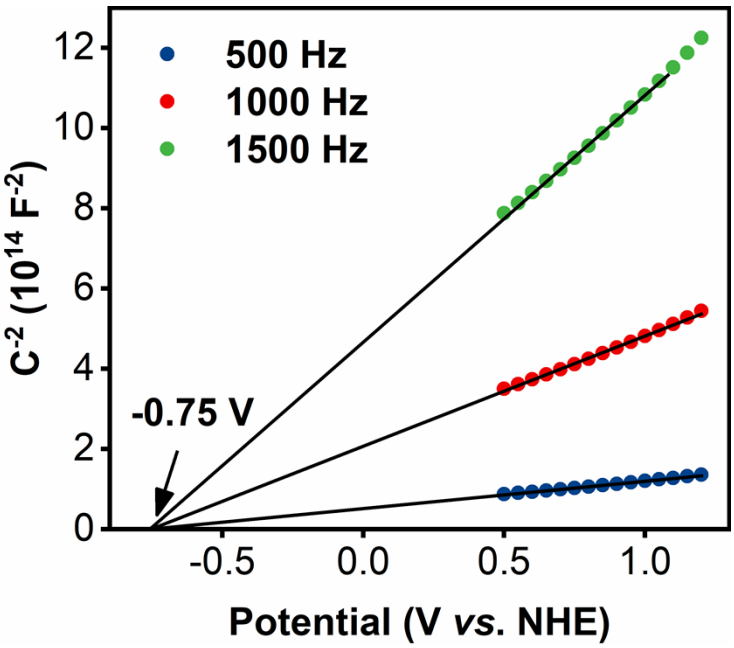


Figure S21. Mott−Schottky plots for PyG-Im-COF.

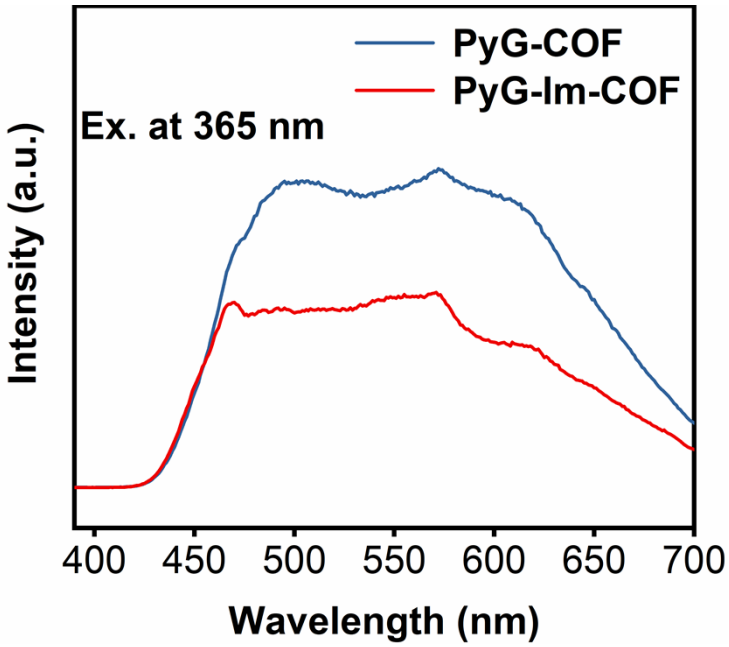


Figure S22. PL spectra of PyG-COF and PyG-Im-COF.

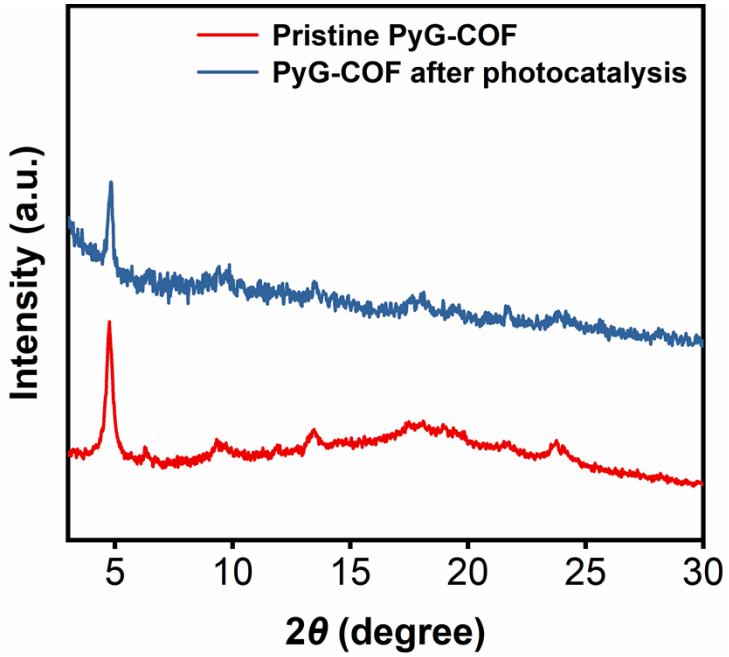


Figure S23. PXRD patterns of PyG-COF before and after photocatalysis.

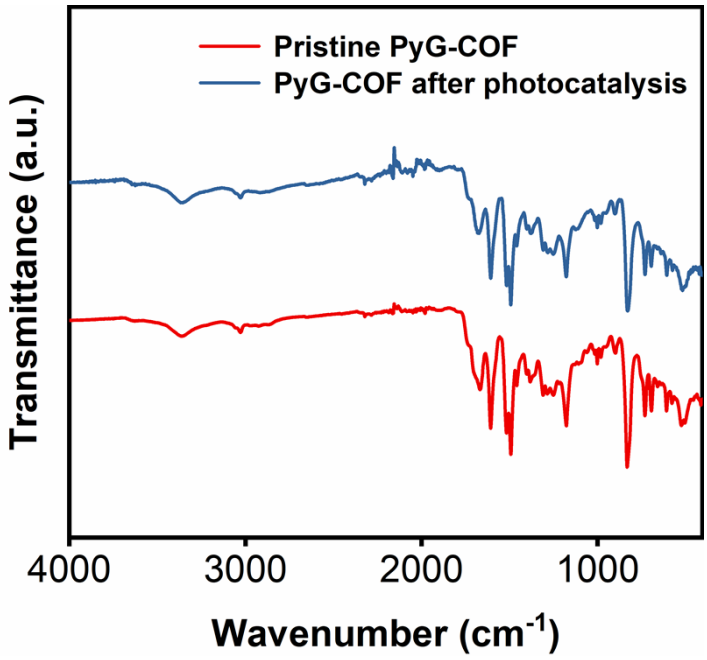


Figure S24. FT-IR spectra of PyG-COF before and after photocatalysis.

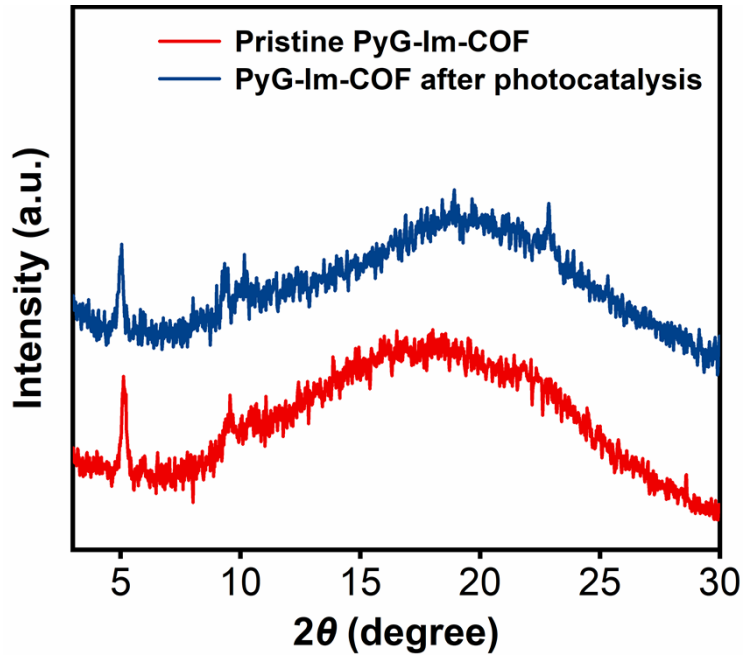


Figure S25. PXRD patterns of PyG-Im-COF before and after photocatalysis.

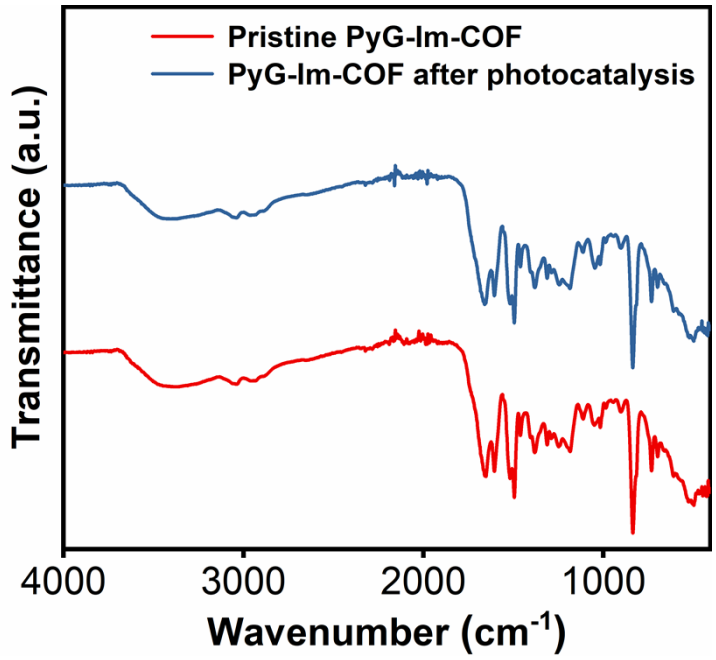


Figure S26. FT-IR spectra of PyG-Im-COF before and after photocatalysis.

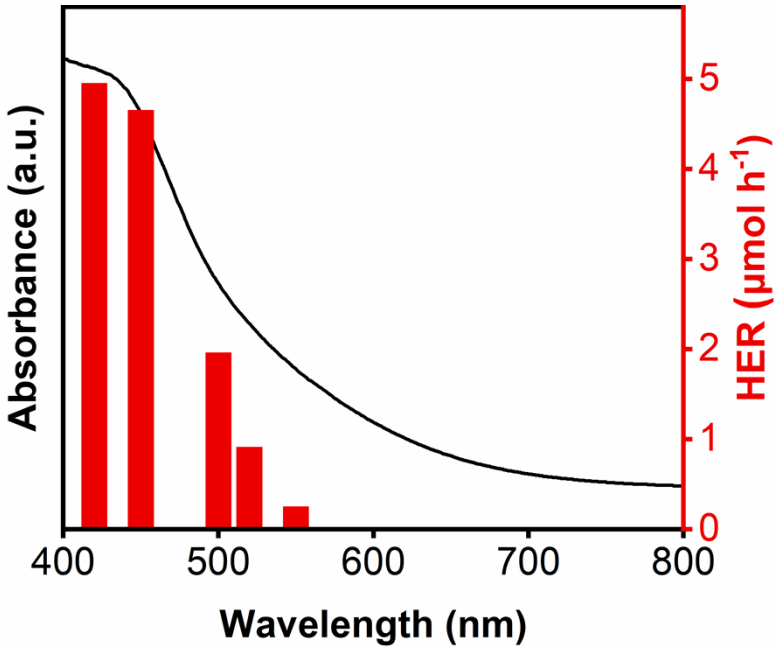


Figure S27. The photocatalytic H_2 evolution rate of PyG-Im-COF under different wavelength monochromatic light.

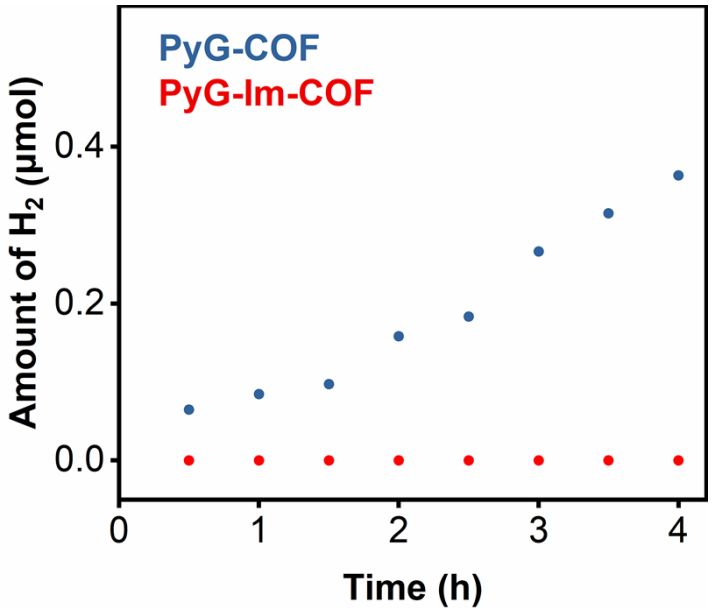


Figure S28. The photocatalytic H_2 evolution performances of PyG-COF and PyG-Im-COF with triethanolamine as the sacrificial electron donor under visible light irradiation.

Table S1. Fractional atomic coordinates for the structural model 1 of PyG-COF in AA stacking.

The structural model 1 of PyG-COF in AA stacking							
a = 27.45 Å, b = 28.74 Å, c = 3.50 Å, $\alpha = \beta$ = 90°, γ = 88.43°							
C1	0.11008	0.47058	0.05681	C77	-0.29686	-0.35426	0.89357
C2	0.04848	0.51434	0.03061	C78	-0.33980	-0.31429	0.86287
C3	0.09449	0.55993	0.05188	C79	-0.37380	-0.32128	0.81513
C4	0.02861	0.60239	0.02517	C80	-0.36714	-0.36876	0.79841
C5	0.21494	0.47227	0.10436	C81	-0.32323	-0.4085	0.82916
C6	0.25367	0.51780	0.12436	C82	-0.21427	-0.5352	0.91436
C7	0.19871	0.56175	0.09950	C83	-0.11000	-0.53319	0.96187
C8	0.27762	0.42817	0.13502	C84	-0.04649	-0.57563	0.98862
C9	0.24629	0.60777	0.12551	C85	0.05827	0.42621	0.03502
C10	0.23172	0.60633	0.17439	C86	-0.26169	-0.58128	0.88842
C11	0.26834	0.64882	0.19954	C87	-0.24302	-0.57995	0.83955
C12	0.32185	0.69386	0.17620	C88	-0.27753	-0.62251	0.81446
C13	0.34265	0.69562	0.12770	C89	-0.33299	-0.66749	0.83783
C14	0.30726	0.65299	0.10269	C90	-0.35835	-0.66912	0.88630
C15	0.37185	0.38287	0.11669	C91	-0.32503	-0.62643	0.91126
C16	0.41503	0.34167	0.14557	N92	-0.34874	-0.71207	0.81330
C17	0.36849	0.34496	0.19383	C93	-0.44612	-0.24059	0.70851
C18	0.28476	0.39009	0.21268	C94	-0.44512	-0.28350	0.7397
C19	0.24055	0.43132	0.18356	N95	-0.38723	-0.19734	0.72396
N20	0.34082	0.73837	0.20080	N96	-0.39684	-0.27971	0.78414
C21	0.33956	0.73976	0.24573	H97	0.29732	0.62571	0.02713
C22	0.34117	-0.21352	0.26838	H98	-0.21433	0.62387	0.04126

C23	0.06226	0.01248	0.48299	H99	0.33360	0.52032	0.16267
C24	0.12266	0.05627	0.45666	H100	0.18948	0.57009	0.19403
C25	0.22547	0.05439	0.40898	H101	0.25482	0.64701	0.23918
C26	0.26666	0.00863	0.38941	H102	0.38869	0.73196	0.10837
C27	0.07494	0.10060	0.47865	H103	0.32860	0.65529	0.06311
C28	0.28385	0.09800	0.37728	H104	0.41428	0.37938	0.07760
C29	0.29686	0.14574	0.39357	H105	0.48848	0.30510	0.12999
C30	0.33980	0.18571	0.36287	H106	0.25227	0.39338	0.25193
C31	0.37380	0.17872	0.31513	H107	0.17359	0.46784	0.19964
C32	0.36714	0.13124	0.29841	H108	0.33719	0.70442	0.26749
C33	0.32323	0.09150	0.32916	H109	0.33577	-0.17820	0.24658
C34	0.21427	-0.0352	0.41436	H110	0.34709	0.00578	0.35115
C35	0.11000	-0.03319	0.46187	H111	0.12120	0.13636	0.45833
C36	0.04649	-0.07563	0.48862	H112	0.27222	0.15238	0.43243
C37	-0.05827	-0.07379	0.53502	H113	0.34716	0.22418	0.37679
C38	0.26169	-0.08128	0.38842	H114	0.39770	0.12503	0.25953
C39	0.24302	-0.07995	0.33955	H115	0.31954	0.05324	0.31472
C40	0.27753	-0.12251	0.31446	H116	0.08061	-0.11278	0.47235
C41	0.33299	-0.16749	0.33783	H117	-0.10407	-0.10898	0.55626
C42	0.35835	-0.16912	0.38630	H118	0.19915	-0.04376	0.31989
C43	0.32503	-0.12643	0.41126	H119	0.26069	-0.12081	0.27484
N44	0.34874	-0.21207	0.31330	H120	0.40644	-0.20541	0.40565
C45	0.44612	0.25941	0.20851	H121	0.35004	-0.12862	0.45081
C46	0.44512	0.2165	0.23970	H122	0.49948	0.25524	0.16970
N47	0.38723	0.30266	0.22396	H123	0.48740	0.17871	0.22506
N48	0.39684	0.22029	0.28414	H124	-0.06162	0.13906	0.54239
C49	-0.11008	-0.02942	0.55681	H125	-0.33360	0.02032	0.66267
C50	-0.04848	0.01434	0.53061	H126	-0.18948	0.07009	0.69403
C51	-0.09449	0.05993	0.55188	H127	-0.25482	0.14701	0.73918
C52	-0.02861	0.10239	0.52517	H128	-0.38869	0.23196	0.60837
C53	-0.21494	-0.02773	0.60436	H129	-0.32860	0.15529	0.56311
C54	-0.25367	0.0178	0.62436	H130	-0.41428	-0.12062	0.5776
C55	-0.19871	0.06175	0.59950	H131	-0.48848	-0.19490	0.62999
C56	-0.27762	-0.07183	0.63502	H132	-0.25227	-0.10662	0.75193
C57	-0.24629	0.10777	0.62551	H133	-0.17359	-0.03216	0.69964
C58	-0.23172	0.10633	0.67439	H134	-0.33719	0.20442	0.76749
C59	-0.26834	0.14882	0.69954	H135	-0.33577	-0.67820	0.74658
C60	-0.32185	0.19386	0.67620	H136	-0.34709	-0.49422	0.85115
C61	-0.34265	0.19562	0.62770	H137	-0.35296	-0.37814	0.97427
C62	-0.30726	0.15299	0.60269	H138	0.15890	-0.37736	0.96020
C63	-0.37185	-0.11713	0.61669	H139	-0.27222	-0.34762	0.93243
C64	-0.41503	-0.15833	0.64557	H140	-0.34716	-0.27582	0.87679
C65	-0.36849	-0.15504	0.69383	H141	-0.39770	-0.37497	0.75953
C66	-0.28476	-0.10991	0.71268	H142	-0.31954	-0.44676	0.81472
C67	-0.24055	-0.06868	0.68356	H143	0.18125	-0.59758	0.97010

N68	-0.34082	0.23837	0.70080	H144	-0.31825	-0.59852	0.98971
C69	-0.33956	0.23976	0.74573	H145	-0.16350	0.40462	0.05605
C70	-0.34117	-0.71352	0.76838	H146	0.33605	0.40454	0.03649
C71	-0.06226	-0.48752	0.98299	H147	-0.19915	-0.54376	0.81989
C72	-0.12266	-0.44373	0.95666	H148	-0.26069	-0.62081	0.77484
C73	-0.22547	-0.44561	0.90898	H149	-0.40644	-0.70541	0.90565
C74	-0.26666	-0.49137	0.88941	H150	-0.35004	-0.62862	0.95081
C75	-0.07494	-0.39940	0.97865	H151	-0.49948	-0.24476	0.6697
C76	-0.28385	-0.40200	0.87728	H152	-0.4874	-0.32129	0.72506

Table S2. Fractional atomic coordinates for the structural model 2 of PyG-COF in AA stacking.

The structural model 2 of PyG-COF in AA stacking							
a = 29.85 Å, b = 26.09 Å, c = 3.18 Å, $\alpha = \beta = 90°$, $\gamma = 90.44°$							
C1	1.40510	-1.01823	-0.03063	C78	1.87524	-1.67888	0.10067
C2	1.44993	-1.04360	0.00331	C79	1.89975	-1.63763	0.11383
C3	1.49831	-1.02089	0.00690	C80	1.85096	-1.39093	0.11283
C4	1.54374	-1.04685	0.01350	C81	1.81491	-1.35908	0.03777
C5	1.59136	-1.02504	-0.02126	C82	1.76426	-1.3718	-0.03106
C6	1.44724	-1.09120	-0.04997	C83	1.75183	-1.41705	-0.06234
C7	1.49332	-1.11268	-0.11805	C84	1.79057	-1.44901	-0.05569
C8	1.54149	-1.09442	-0.03022	N85	1.69757	-1.22598	0.00900
C9	1.40171	-1.11926	-0.04244	C86	1.68908	-1.26850	-0.00215
C10	1.5833	-1.12576	-0.00085	C87	1.7319	-1.29712	-0.03029
C11	1.57106	-1.17108	0.08945	N88	1.72426	-1.33990	-0.03172
C12	1.60722	-1.20422	0.08064	C89	1.22421	-1.19538	0.02504
C13	1.65887	-1.19320	0.03004	C90	1.18851	-1.23211	0.02701
C14	1.67343	-1.14899	-0.01910	N91	1.27227	-1.20553	0.04124
C15	1.63656	-1.11629	-0.06075	N92	1.20796	-1.27183	0.03942
C16	1.35136	-1.10431	-0.12627	N93	1.79571	-1.72210	-0.00654
C17	1.30879	-1.13073	-0.05871	N94	1.72920	-1.78781	-0.03461
C18	1.31469	-1.17591	0.02370	C95	1.77730	-1.79838	-0.02005
C19	1.36337	-1.19376	0.06295	C96	1.81407	-1.76216	-0.00770
C20	1.40607	-1.16573	0.05151	H97	1.37139	-1.03056	0.13235
C21	1.10287	-1.44290	0.04514	H98	1.39368	-1.02263	-0.32294
C22	1.04860	-1.44979	0.03926	H99	1.60435	-1.0332	-0.30247
C23	1.02687	-1.49317	-0.00828	H100	1.62300	-1.03808	0.15241
C24	1.06002	-1.53008	-0.05644	H101	1.49184	-1.14477	-0.26762
C25	1.11352	-1.52456	0.00724	H102	1.53290	-1.18233	0.16609
C26	1.13231	-1.48148	0.08483	H103	1.59357	-1.23809	0.11845
C27	1.01409	-1.41132	-0.00082	H104	1.71364	-1.14030	-0.05536
C28	1.03832	-1.57064	-0.18229	H105	1.65325	-1.08630	-0.17726
C29	1.13077	-1.39739	0.01736	H106	1.34157	-1.07403	-0.27663
C30	1.15217	-1.56158	0.00371	H107	1.27162	-1.11583	-0.09993
C31	1.18456	-1.39351	0.08416	H108	1.36819	-1.22944	0.10944

C32	1.20936	-1.35214	0.07701	H109	1.44207	-1.18139	0.12325
C33	1.18137	-1.31316	0.03112	H110	1.17113	-1.47885	0.17995
C34	1.12956	-1.31562	-0.05243	H111	1.01883	-1.40312	-0.29753
C35	1.10665	-1.35684	-0.09921	H112	1.02404	-1.38043	0.16108
C36	1.13977	-1.60566	0.12148	H113	1.06035	-1.59814	-0.28375
C37	1.17585	-1.63911	0.11452	H114	1.20977	-1.42117	0.13362
C38	1.22672	-1.62866	0.02019	H115	1.25062	-1.35037	0.11080
C39	1.24096	-1.58497	-0.06906	H116	1.10696	-1.28620	-0.11334
C40	1.20398	-1.55214	-0.09572	H117	1.07165	-1.35364	-0.25853
C41	1.30086	-1.73177	-0.01349	H118	1.10267	-1.61572	0.22190
C42	1.25712	-1.70376	-0.01748	H119	1.16372	-1.67260	0.19747
N43	1.26539	-1.66139	0.01547	H120	1.28072	-1.57687	-0.13122
C44	1.59401	-1.97548	0.01572	H121	1.21686	-1.51953	-0.19669
C45	1.54931	-1.94995	-0.01620	H122	1.33788	-1.71633	0.03582
C46	1.5009	-1.97261	-0.00940	H123	1.21924	-1.71821	-0.05488
C47	1.45547	-1.94674	-0.00377	H124	1.60612	-1.96957	0.30362
C48	1.40782	-1.96886	0.03345	H125	1.62751	-1.96447	-0.15409
C49	1.55253	-1.90218	0.03290	H126	1.37560	-1.95445	-0.13006
C50	1.50650	-1.88047	0.10909	H127	1.39675	-1.96327	0.32471
C51	1.45788	-1.89918	0.04458	H128	1.50826	-1.84814	0.25376
C52	1.59864	-1.87438	0.02030	H129	1.46305	-1.81104	-0.16138
C53	1.41545	-1.86842	0.03032	H130	1.39795	-1.75771	-0.16286
C54	1.42539	-1.82318	-0.07856	H131	1.28462	-1.85923	0.09405
C55	1.38692	-1.79180	-0.09470	H132	1.34957	-1.90847	0.26693
C56	1.33579	-1.80498	-0.03900	H133	1.66029	-1.92062	0.22134
C57	1.32419	-1.84903	0.04828	H134	1.72914	-1.8782	0.06289
C58	1.36320	-1.87912	0.11624	H135	1.63267	-1.76364	-0.09654
C59	1.64941	-1.88978	0.08682	H136	1.55856	-1.81144	-0.12213
C60	1.69201	-1.86301	0.02916	H137	1.83069	-1.52279	0.21943
C61	1.68637	-1.81741	-0.03192	H138	1.97395	-1.60959	-0.28921
C62	1.63753	-1.79949	-0.06368	H139	1.94974	-1.41150	0.34610
C63	1.59459	-1.82753	-0.05901	H140	1.94029	-1.39099	-0.11214
N64	1.29468	-1.77434	-0.05024	H141	1.79936	-1.57284	-0.18805
C65	1.89958	-1.55275	0.00525	H142	1.75559	-1.64415	-0.14510
C66	1.95239	-1.54414	-0.07011	H143	1.89682	-1.70838	0.17929
C67	1.97234	-1.50013	-0.02777	H144	1.93854	-1.63809	0.21496
C68	1.93752	-1.46414	-0.00363	H145	1.88304	-1.37676	0.26398
C69	1.88384	-1.47210	0.04307	H146	1.82736	-1.32476	0.07111
C70	1.86831	-1.51639	0.09752	H147	1.71218	-1.42738	-0.09507
C71	1.98625	-1.57751	-0.18723	H148	1.77896	-1.48309	-0.11689
C72	1.95843	-1.41847	0.05198	H149	1.65142	-1.28339	0.00651
C73	1.87421	-1.59805	0.00200	H150	1.76923	-1.28147	-0.04557
C74	1.84209	-1.43679	0.03461	H151	1.21026	-1.16152	0.00401
C75	1.82160	-1.60152	-0.09637	H152	1.14788	-1.22572	0.01522
C76	1.79627	-1.6424	-0.08065	H153	1.79078	-1.83245	-0.01434

C77	1.82327	-1.68119	0.00384	H154	1.85468	-1.76899	-0.00603

Table S3. Fractional atomic coordinates for the structural model 3 of PyG-COF in AA stacking.

The structural model 3 of PyG-COF in AA stacking							
a = 26.60 Å, b = 29.15 Å, c = 3.59 Å, α = 89.18°, β =90.48°, γ = 89.68°							
C1	-1.87332	2.35477	-1.91198	C78	-1.02848	2.52136	-0.99278
C2	-1.91719	2.63165	-1.90834	C79	-1.10678	2.54861	-1.03353
C3	-1.96380	2.61156	-1.86396	C80	-1.18027	2.52189	-1.0736
C4	-1.92017	2.64171	-1.82520	C81	-1.17020	2.46975	-1.07432
C5	-1.83193	2.69285	-1.83008	C82	-1.04956	2.62607	-0.99121
C6	-1.78671	2.71346	-1.87425	C83	-1.11332	2.60187	-1.03286
C7	-1.82931	2.68319	-1.91289	C84	-1.13094	2.35758	-1.07783
C8	-1.78499	2.30364	-1.91780	C85	-1.96052	2.54737	-1.95130
C9	-1.74054	2.27177	-1.88007	C86	-1.97544	2.60052	-1.95033
C10	-1.78389	2.29020	-1.83555	C87	-1.94065	2.44065	-1.95271
C11	-1.87351	2.34104	-1.82919	C88	-1.86546	2.46742	-1.91268
C12	-1.91872	2.37279	-1.86705	C89	-1.87450	2.51954	-1.91204
C13	-1.59703	2.10480	-1.52686	C90	-2.00114	2.36313	-1.99491
C14	-1.59883	2.05162	-1.53030	C91	-1.93667	2.38735	-1.95323
C15	-1.52572	2.02158	-1.49114	C92	-1.68428	2.80077	-1.74985
C16	-1.45729	2.04467	-1.44832	C93	-1.72206	2.77093	-1.79159
C17	-1.46932	2.09775	-1.44441	N94	-1.79261	2.72302	-1.78983
C18	-1.53567	2.12618	-1.48388	C95	-1.36356	2.18834	-1.23599
C19	-1.67491	2.02769	-1.57176	C96	-1.32566	2.21816	-1.19426
C20	-1.37475	2.01404	-1.41070	H97	-2.03836	2.57008	-1.85910
C21	-1.65385	2.14001	-1.56635	H98	-1.95651	2.62464	-1.78943
C22	-1.42311	2.12557	-1.40033	H99	-1.71490	2.75507	-1.87873
C23	-1.74358	2.19076	-1.55819	H100	-1.79196	2.70074	-1.94845
C24	-1.78137	2.22489	-1.59448	H101	-1.74859	2.28764	-1.95378
C25	-1.72920	2.20906	-1.63969	H102	-1.66857	2.23053	-1.88554
C26	-1.63979	2.15856	-1.64818	H103	-1.90968	2.35657	-1.79304
C27	-1.60113	2.12466	-1.61188	H104	-1.99353	2.41385	-1.86106
C28	-1.47742	2.10177	-1.35774	H105	-1.53833	2.16878	-1.47983
C29	-1.44487	2.12846	-1.31690	H106	-1.74270	2.05095	-1.60351
C30	-1.35991	2.18008	-1.31777	H107	-1.58143	2.02393	-1.38191
C31	-1.30777	2.20435	-1.35999	H108	-1.07952	2.02330	-1.39817
C32	-1.33939	2.17739	-1.40086	H109	-1.78656	2.20456	-1.52155
N33	-1.73949	2.25638	-1.79765	H110	-1.85493	2.26574	-1.58717
C34	-1.77287	2.26987	-1.75524	H111	-1.59830	2.14503	-1.68493
C35	-1.72732	2.23251	-1.71900	H112	-1.52557	2.08399	-1.61967
N36	-1.76864	2.24472	-1.67637	H113	-1.54945	2.05994	-1.35607
N37	-1.32433	2.20848	-1.27636	H114	-1.48736	2.10834	-1.28256
C38	-1.17811	2.63462	-1.07389	H115	-1.23915	2.24629	-1.36127
C39	-1.08318	2.37757	-1.12220	H116	-1.29622	2.19803	-1.43494

C40	-1.12477	2.34727	-1.16084	H117	-1.83733	2.31065	-1.74648
C41	-1.21292	2.29616	-1.15589	H118	-1.65457	2.19208	-1.72813
C42	-1.25913	2.27563	-1.11171	H119	-1.00940	2.41907	-1.12711
C43	-1.21852	2.30605	-1.07320	H120	-1.08683	2.36418	-1.19665
C44	-1.26361	2.68580	-1.06779	H121	-1.33004	2.23400	-1.10719
C45	-1.30645	2.71791	-1.10539	H122	-1.25631	2.28925	-1.03735
C46	-1.26429	2.69972	-1.15000	H123	-1.29892	2.7016	-1.03172
C47	-1.17956	2.64876	-1.15658	H124	-1.37619	2.7592	-1.09975
C48	-1.13629	2.61674	-1.11888	H125	-1.14576	2.63334	-1.1928
N49	-1.25114	2.26590	-1.19610	H126	-1.06603	2.57557	-1.12507
C50	-1.45581	2.88495	-1.45896	H127	-1.51576	2.82099	-1.50602
C51	-1.45140	2.93815	-1.45559	H128	-1.08356	2.94875	-1.40292
C52	-1.52237	2.96822	-1.49479	H129	-1.58592	2.94941	-1.38689
C53	-1.58928	2.94513	-1.53765	H130	-1.73372	2.95801	-1.60994
C54	-1.57799	2.89207	-1.54159	H131	-1.28110	2.78474	-1.46397
C55	-1.51590	2.86360	-1.50200	H132	-1.20699	2.72400	-1.39811
C56	-1.37237	2.96205	-1.41427	H133	-1.44368	2.84551	-1.30053
C57	-1.67004	2.97570	-1.57534	H134	-1.52098	2.90625	-1.36603
C58	-1.40226	2.84976	-1.41934	H135	-1.48457	2.92930	-1.63012
C59	-1.62271	2.86417	-1.58569	H136	-1.54710	2.88052	-1.70352
C60	-1.31738	2.79889	-1.42734	H137	-1.81837	2.74353	-1.62440
C61	-1.27623	2.76501	-1.39092	H138	-1.76004	2.79206	-1.55094
C62	-1.31967	2.78122	-1.34569	H139	-1.20072	2.68003	-1.23907
C63	-1.40668	2.83177	-1.33728	H140	-1.37692	2.79882	-1.25703
C64	-1.44838	2.86546	-1.37375	H141	-1.34241	2.51973	-0.98399
C65	-1.56220	2.88765	-1.62835	H142	-1.25016	2.54292	-1.10654
C66	-1.59549	2.86075	-1.66911	H143	-1.23258	2.44963	-1.10783
C67	-1.68853	2.80928	-1.66812	H144	-1.30321	2.65106	-0.98425
C68	-1.74522	2.78533	-1.62582	H145	-0.79320	2.65196	-0.99493
C69	-1.71258	2.81247	-1.58505	H146	-2.27325	2.54503	-1.94197
N70	-1.30467	2.73391	-1.18776	H147	-1.66046	2.60266	-1.95842
C71	-1.26750	2.72071	-1.23018	H148	-1.79507	2.44641	-1.87974
C72	-1.31167	2.75820	-1.26630	H149	-1.80993	2.53966	-1.87860
N73	-1.27731	2.74572	-1.30897	H150	-1.99657	2.32033	-1.99667
N74	-1.72450	2.78072	-1.70945	H151	-1.61781	2.84262	-1.75350
C75	-1.01792	2.46790	-0.99351	H152	-1.68942	2.78974	-1.82668
C76	-1.0857	2.44193	-1.03502	H153	-1.42916	2.14646	-1.23239
C77	-1.07314	2.38872	-1.03589	H154	-1.36314	2.19853	-1.15961

Table S4. Fractional atomic coordinates for the structural model 4 of PyG-COF in AA stacking.

The structural model 4 of PyG-COF in AA stacking							
a = 24.75 Å, b = 27.53 Å, c = 3.77 Å, $\alpha = \gamma = 90°$, $\beta = 92.56°$							
C1	1.58751	-0.98285	3.81132	C21	1.92399	-0.68938	5.08578
C2	1.54461	-0.95652	3.65493	N22	1.79277	-0.73082	4.66131

C3	1.54473	-0.90530	3.65468	H23	1.62347	-0.96294	3.94116
C4	1.58941	-0.87507	3.81609	H24	1.46190	-0.81017	3.14714
C5	1.42021	-0.82665	3.09284	H25	1.38779	-0.75896	2.86321
C6	1.37921	-0.79811	2.93550	H26	1.27549	-0.88131	2.91130
C7	1.32776	-0.81743	2.86665	H27	1.34898	-0.93241	3.19753
C8	1.31751	-0.86538	2.96255	H28	1.77018	-0.84396	4.31998
C9	1.35843	-0.89362	3.12011	H29	1.84423	-0.79043	4.63263
C10	1.76089	-0.80487	4.39007	H30	1.87655	-0.55269	5.05595
C11	1.80227	-0.77500	4.56963	H31	1.84919	-0.58486	5.15125
N12	1.71318	-0.78822	4.30622	H32	1.77867	-0.63869	4.85488
C13	1.95549	-0.55915	5.34261	H33	1.89532	-0.75816	4.85723
C14	1.95569	-0.61028	5.33957	H34	1.96582	-0.70479	5.15359
C15	1.91252	-0.53294	5.18725	C35	1.50000	-0.98210	3.50000
C16	1.91240	-0.64107	5.16758	C36	1.50000	-0.88124	3.50000
C17	1.86011	-0.62371	5.08463	H37	1.50000	-0.84008	3.50000
C18	1.82085	-0.65346	4.92036	C38	1.00000	-0.53354	1.50000
C19	1.83315	-0.70123	4.83622	C39	1.00000	-0.63413	1.50000
C20	1.88501	-0.71911	4.92195	H40	1.00000	-0.67528	1.50000

Table S5. Fractional atomic coordinates for the structural model 5 of PyG-COF in AA stacking.

The structural model 5 of PyG-COF in AA stacking							
$a = b = 28.06$ Å, $c = 3.39$ Å, $\alpha = \beta = \gamma = 90°$							
C1	1.40478	-1.02970	-0.10069	C78	1.88059	-1.6896	-0.06602
C2	1.44975	-1.05717	0.01394	C79	1.90517	-1.64138	0.00471
C3	1.49785	-1.03083	0.05940	C80	1.90006	-1.35535	-0.09598
C4	1.54298	-1.05752	0.16154	C81	1.87290	-1.30843	-0.03390
C5	1.59126	-1.03043	0.15411	C82	1.82447	-1.30897	0.17837
C6	1.44618	-1.11024	0.11801	C83	1.80315	-1.35583	0.33136
C7	1.49148	-1.1373	0.23162	C84	1.82935	-1.40283	0.25594
C8	1.53962	-1.11129	0.23652	C85	1.78479	-1.81115	0.16140
C9	1.39802	-1.13651	0.11909	C86	1.82123	-1.78172	-0.07037
C10	1.58450	-1.14079	0.25896	N87	1.73752	-1.78789	0.24828
C11	1.58015	-1.19483	0.20342	N88	1.80321	-1.73710	-0.26713
C12	1.62386	-1.22254	0.06754	C89	1.18968	-1.78530	0.21921
C13	1.67215	-1.19600	-0.10250	C90	1.22172	-1.80910	-0.08960
C14	1.67696	-1.14375	0.13898	N91	1.20731	-1.74023	0.41166
C15	1.63319	-1.11604	0.27301	N92	1.26694	-1.78391	-0.20841
C16	1.35214	-1.11187	-0.02614	C93	1.80477	-1.22393	-0.07485
C17	1.30390	-1.13739	0.01237	C94	1.76157	-1.20165	-0.27885
C18	1.30174	-1.18795	0.18554	N95	1.79540	-1.26439	0.20497
C19	1.34771	-1.21350	0.31367	N96	1.71390	-1.22573	-0.22617
C20	1.39593	-1.18788	0.27719	H97	1.37329	-1.04206	0.08541
C21	1.11935	-1.45435	0.00330	H98	1.39685	-1.03384	-0.42907
C22	1.06464	-1.45483	0.03100	H99	1.61700	-1.05124	-0.04109

C23	1.03778	-1.50174	-0.02636	H100	1.60621	-1.02998	0.46711
C24	1.06443	-1.54936	-0.04129	H101	1.48972	-1.17705	0.29999
C25	1.11925	-1.54950	-0.01968	H102	1.54416	-1.21331	0.23516
C26	1.14682	-1.50191	-0.01510	H103	1.62157	-1.26241	0.00539
C27	1.03593	-1.40873	0.10500	H104	1.71355	-1.12611	0.13177
C28	1.03577	-1.59635	-0.04544	H105	1.63638	-1.07710	0.36378
C29	1.14585	-1.40656	-0.03063	H106	1.35375	-1.07496	-0.16422
C30	1.14587	-1.59698	0.02867	H107	1.26986	-1.11903	-0.09074
C31	1.19388	-1.40414	-0.24876	H108	1.34603	-1.25139	0.43430
C32	1.21351	-1.35544	-0.38001	H109	1.43005	-1.20665	0.37333
C33	1.18622	-1.30957	-0.27363	H110	1.18744	-1.50193	-0.02055
C34	1.14244	-1.31186	-0.00204	H111	1.05726	-1.37598	0.01658
C35	1.12223	-1.36052	0.11972	H112	1.02762	-1.40705	0.43422
C36	1.12267	-1.64355	-0.11415	H113	1.05492	-1.63206	-0.04179
C37	1.14410	-1.69170	0.00658	H114	1.21340	-1.43832	-0.33223
C38	1.18859	-1.69303	0.27063	H115	1.24769	-1.35337	-0.56117
C39	1.21453	-1.64654	0.38077	H116	1.12425	-1.27765	0.09921
C40	1.19377	-1.59833	0.24941	H117	1.08894	-1.36249	0.31189
C41	1.21045	-1.19017	0.04810	H118	1.08924	-1.64235	-0.30495
C42	1.18172	-1.21689	-0.26693	H119	1.12655	-1.72632	-0.09291
N43	1.25478	-1.21359	0.20744	H120	1.24880	-1.64783	0.56121
N44	1.2024	-1.26222	-0.43314	H121	1.21254	-1.56372	0.33232
C45	1.59739	-1.97416	-0.07617	H122	1.19963	-1.15288	0.14742
C46	1.55007	-1.94655	-0.06231	H123	1.14627	-1.20231	-0.37871
C47	1.50270	-1.97362	-0.02833	H124	1.62244	-1.95941	0.15893
C48	1.45533	-1.94618	-0.01702	H125	1.61438	-1.96924	-0.37924
C49	1.40804	-1.97349	0.01775	H126	1.38354	-1.96246	-0.23473
C50	1.55021	-1.89181	-0.05369	H127	1.39035	-1.96400	0.31048
C51	1.50279	-1.86422	-0.06259	H128	1.5029	-1.82361	-0.07226
C52	1.45525	-1.89156	-0.05447	H129	1.44348	-1.79198	-0.25497
C53	1.59755	-1.86476	-0.01145	H130	1.36086	-1.74526	-0.34912
C54	1.40786	-1.86428	-0.09004	H131	1.27764	-1.88234	-0.01683
C55	1.40820	-1.81124	-0.20564	H132	1.35953	-1.92875	0.08003
C56	1.36079	-1.78446	-0.26085	H133	1.64612	-1.92904	-0.18215
C57	1.31330	-1.81056	-0.19039	H134	1.72785	-1.88466	-0.01610
C58	1.31292	-1.86331	-0.07205	H135	1.64375	-1.74778	0.30744
C59	1.36011	-1.89008	-0.01899	H136	1.56163	-1.79225	0.14073
C60	1.64540	-1.89090	-0.06847	H137	1.83503	-1.49451	0.07535
C61	1.69244	-1.86534	0.02441	H138	1.95965	-1.62968	-0.03905
C62	1.69158	-1.81350	0.16843	H139	1.96830	-1.37395	-0.02162
C63	1.64403	-1.78657	0.20737	H140	1.99669	-1.40359	-0.45372
C64	1.59695	-1.81200	0.11048	H141	1.80861	-1.56156	-0.33793
C65	1.90040	-1.54447	-0.00405	H142	1.76633	-1.64557	-0.47177
C66	1.95487	-1.54681	-0.03338	H143	1.89978	-1.72423	0.00978
C67	1.98358	-1.50047	-0.04424	H144	1.94288	-1.64008	0.12966

C68	1.95844	-1.45215	-0.06376	H145	1.93560	-1.35535	-0.25846
C69	1.90423	-1.44988	-0.00051	H146	1.88828	-1.27347	-0.14865
C70	1.87527	-1.49614	0.03098	H147	1.76732	-1.35582	0.49009
C71	1.98089	-1.59504	-0.04123	H148	1.81305	-1.43798	0.35737
C72	1.98851	-1.40680	-0.12502	H149	1.79287	-1.84913	0.26051
C73	1.87104	-1.59032	0.00001	H150	1.86024	-1.79282	-0.09006
C74	1.87815	-1.4024	0.05062	H151	1.15376	-1.80138	0.30276
C75	1.82802	-1.59618	-0.26592	H152	1.21277	-1.84589	-0.21181
C76	1.80383	-1.64432	-0.34279	H153	1.84256	-1.21134	-0.14128
C77	1.82967	-1.69082	-0.23371	H154	1.76501	-1.16719	-0.45500

Table S6. Fractional atomic coordinates for the structural model 6 of PyG-COF in AA stacking.

The structural model 6 of PyG-COF in AA stacking							
a = 23.23 Å, b = 30.83 Å, c = 3.74 Å, $\alpha = \beta = 90°$, $\gamma = 86.19°$							
C1	0.21130	0.40881	-0.97745	C78	0.57323	0.55304	-0.04547
C2	0.37872	0.45497	-0.95171	C79	0.59258	0.55235	-0.09134
C3	0.50841	0.50200	-0.97442	C80	0.50840	0.50200	-0.11290
C4	0.63810	0.54903	-0.95171	C81	0.41371	0.39657	-0.01955
C5	0.80553	0.59519	-0.97745	C82	0.60311	0.60743	-0.01955
C6	0.38487	0.45431	-0.90586	C83	0.31329	0.40255	-0.11850
C7	0.50841	0.50200	-0.88418	C84	0.70352	0.60145	-0.11850
C8	0.63195	0.54969	-0.90586	C85	0.22755	0.41208	-0.16244
C9	0.26043	0.40620	-0.87899	C86	0.11195	0.36782	-0.18842
C10	0.75636	0.59779	-0.87899	C87	0.07930	0.31268	-0.17095
C11	0.85987	0.58743	-0.83574	C88	0.16676	0.30252	-0.12748
C12	0.97286	0.63186	-0.80973	C89	0.28177	0.34703	-0.10157
C13	0.98319	0.68787	-0.82647	C90	0.73503	0.65697	-0.10157
C14	0.87643	0.69875	-0.86926	C91	0.85005	0.70148	-0.12747
C15	0.76331	0.65416	-0.89522	C92	0.93750	0.69132	-0.17095
C16	0.25351	0.34984	-0.89522	C93	0.90484	0.63618	-0.18842
C17	0.14039	0.30525	-0.86926	C94	0.78922	0.59191	-0.16244
C18	0.03363	0.31613	-0.82647	N95	-0.04553	0.26666	-0.19650
C19	0.04396	0.37214	-0.80973	N96	1.06233	0.73734	-0.1965
C20	0.15695	0.41657	-0.83574	H97	-0.07803	0.42356	-0.98521
N21	-0.08386	0.26973	-0.80072	H98	0.21647	0.36740	-0.95756
N22	1.10065	0.73426	-0.80072	H99	1.09486	0.58044	-0.98521
C23	-0.19407	0.27658	-0.76117	H100	0.80036	0.6366	-0.95756
C24	-0.30948	0.22755	-0.73673	H101	0.51132	0.50312	-0.84722
C25	1.21089	0.72742	-0.76117	H102	0.85215	0.54225	-0.82149
C26	1.32630	0.77645	-0.73673	H103	1.05721	0.62272	-0.77474
C27	-0.87592	0.05026	-0.54460	H104	0.88137	0.74417	-0.88314
C28	-0.87691	0.05035	-0.59054	H105	0.67593	0.66402	-0.93000
C29	-0.99159	0.00200	-0.61208	H106	0.34091	0.33998	-0.93000
C30	-0.87450	0.05017	-0.45244	H107	0.13494	0.25975	-0.88298

C31	-0.75583	0.09658	-0.47603	H108	-0.04016	0.38147	-0.77476
C32	-0.75663	0.09665	-0.52104	H109	0.16470	0.46175	-0.82149
C33	-0.99160	0.00200	-0.38496	H110	-0.20081	0.32105	-0.74545
C34	-0.87366	0.05015	-0.40648	H111	-0.30211	0.18304	-0.75240
C35	-0.75817	0.09861	-0.61791	H112	1.21767	0.68296	-0.74544
C36	-0.74864	0.09796	-0.37908	H113	1.31894	0.82096	-0.7524
C37	-0.75652	0.15535	-0.60228	H114	-1.16023	0.07108	-0.54428
C38	-0.64608	0.19976	-0.62860	H115	-0.99458	0.00074	-0.64904
C39	-0.53656	0.18837	-0.67121	H116	-0.65564	0.13545	-0.45831
C40	-0.54136	0.13202	-0.68741	H117	-0.65737	0.13557	-0.53879
C41	-0.65163	0.08775	-0.66102	H118	-0.99476	0.00071	-0.34800
C42	-0.64612	0.08686	-0.33585	H119	-0.84617	0.16570	-0.56765
C43	-0.52750	0.13058	-0.30953	H120	-0.64509	0.24554	-0.61532
C44	-0.50988	0.18663	-0.32593	H121	-0.45499	0.12227	-0.72224
C45	-0.61564	0.19830	-0.36863	H122	-0.65459	0.04228	-0.67485
C46	-0.73431	0.15445	-0.39487	H123	-0.65927	0.04164	-0.32185
N47	-0.42030	0.23459	-0.69723	H124	-0.44456	0.12079	-0.27459
N48	-0.38413	0.23225	-0.30005	H125	-0.60534	0.24379	-0.38222
C49	-0.27532	0.22496	-0.26048	H126	-0.82031	0.16507	-0.42959
C50	-0.15031	0.27349	-0.23627	H127	-0.27757	0.18062	-0.24468
C51	1.89372	0.95365	-0.59054	H128	-0.14458	0.31761	-0.25234
C52	1.89273	0.95374	-0.54460	H129	2.29397	0.98168	-0.5216
C53	2.00841	1.00200	-0.52160	H130	1.67418	0.86843	-0.53879
C54	1.77344	0.90735	-0.52104	H131	1.67377	0.86908	-0.45754
C55	1.77264	0.90742	-0.47603	H132	1.67134	0.96171	-0.67486
C56	1.89131	0.95383	-0.45244	H133	1.47164	0.88156	-0.72226
C57	2.00841	1.00200	-0.47542	H134	1.66242	0.75854	-0.61516
C58	1.89047	0.95385	-0.40648	H135	1.86298	0.8383	-0.56765
C59	1.77498	0.90539	-0.61791	H136	1.83710	0.83893	-0.42959
C60	1.76545	0.90604	-0.37908	H137	1.62159	0.76013	-0.38205
C61	1.66842	0.91624	-0.66102	H138	1.46161	0.88337	-0.27460
C62	1.55818	0.87198	-0.68741	H139	1.67600	0.96235	-0.32184
C63	1.55337	0.81563	-0.67121	H140	1.29436	0.82338	-0.24468
C64	1.66289	0.80424	-0.62860	H141	1.16138	0.68639	-0.25234
C65	1.77333	0.84865	-0.60228	H142	0.51063	0.50334	-0.14986
C66	1.75111	0.84955	-0.39487	H143	0.69359	0.37701	-0.01177
C67	1.63244	0.80570	-0.36863	H144	0.26450	0.36438	-0.03935
C68	1.52669	0.81737	-0.32593	H145	0.32324	0.62700	-0.01177
C69	1.54431	0.87342	-0.30953	H146	0.75233	0.63962	-0.03935
C70	1.66290	0.91713	-0.33585	H147	0.25207	0.45654	-0.17736
N71	1.43711	0.76941	-0.69723	H148	0.04368	0.37641	-0.22397
N72	1.40094	0.77175	-0.30005	H149	0.14447	0.25776	-0.11299
C73	1.29212	0.77904	-0.26048	H150	0.35050	0.33767	-0.06614
C74	1.16711	0.73051	-0.23627	H151	0.66627	0.66633	-0.06614
C75	0.42423	0.45165	-0.09134	H152	0.87282	0.74631	-0.11312

C76	0.44355	0.45095	-0.04547	H153	0.97286	0.62743	-0.22395
C77	0.50841	0.50200	-0.02280	H154	0.76466	0.54745	-0.17735

Table S7. Fractional atomic coordinates for the structural model 7 of PyG-COF in AA stacking.

The structural model 7 of PyG-COF in AA stacking							
a = 25.30 Å, b = 31.33 Å, c = 3.42 Å, $\alpha = \beta = \gamma$ = 90°							
C1	0.21130	0.40881	-0.97745	C78	0.57323	0.55304	-0.04547
C2	0.37872	0.45497	-0.95171	C79	0.59258	0.55235	-0.09134
C3	0.50841	0.50200	-0.97442	C80	0.5084	0.50200	-0.11290
C4	0.63810	0.54903	-0.95171	C81	0.41371	0.39657	-0.01955
C5	0.80553	0.59519	-0.97745	C82	0.60311	0.60743	-0.01955
C6	0.38487	0.45431	-0.90586	C83	0.31329	0.40255	-0.11850
C7	0.50841	0.50200	-0.88418	C84	0.70352	0.60145	-0.11850
C8	0.63195	0.54969	-0.90586	C85	0.22755	0.41208	-0.16244
C9	0.26043	0.4062	-0.87899	C86	0.11195	0.36782	-0.18842
C10	0.75636	0.59779	-0.87899	C87	0.07930	0.31268	-0.17095
C11	0.85987	0.58743	-0.83574	C88	0.16676	0.30252	-0.12748
C12	0.97286	0.63186	-0.80973	C89	0.28177	0.34703	-0.10157
C13	0.98319	0.68787	-0.82647	C90	0.73503	0.65697	-0.10157
C14	0.87643	0.69875	-0.86926	C91	0.85005	0.70148	-0.12747
C15	0.76331	0.65416	-0.89522	C92	0.9375	0.69132	-0.17095
C16	0.25351	0.34984	-0.89522	C93	0.90484	0.63618	-0.18842
C17	0.14039	0.30525	-0.86926	C94	0.78922	0.59191	-0.16244
C18	0.03363	0.31613	-0.82647	N95	-0.04553	0.26666	-0.1965
C19	0.04396	0.37214	-0.80973	N96	1.06233	0.73734	-0.1965
C20	0.15695	0.41657	-0.83574	H97	-0.07803	0.42356	-0.98521
N21	-0.08386	0.26973	-0.80072	H98	0.21647	0.3674	-0.95756
N22	1.10065	0.73426	-0.80072	H99	1.09486	0.58044	-0.98521
C23	-0.19407	0.27658	-0.76117	H100	0.80036	0.63660	-0.95756
C24	-0.30948	0.22755	-0.73673	H101	0.51132	0.50312	-0.84722
C25	1.21089	0.72742	-0.76117	H102	0.85215	0.54225	-0.82149
C26	1.32630	0.77645	-0.73673	H103	1.05721	0.62272	-0.77474
C27	-0.87592	0.05026	-0.54460	H104	0.88137	0.74417	-0.88314
C28	-0.87691	0.05035	-0.59054	H105	0.67593	0.66402	-0.93000
C29	-0.99159	0.00200	-0.61208	H106	0.34091	0.33998	-0.93000
C30	-0.87450	0.05017	-0.45244	H107	0.13494	0.25975	-0.88298
C31	-0.75583	0.09658	-0.47603	H108	-0.04016	0.38147	-0.77476
C32	-0.75663	0.09665	-0.52104	H109	0.16470	0.46175	-0.82149
C33	-0.99160	0.00200	-0.38496	H110	-0.20081	0.32105	-0.74545
C34	-0.87366	0.05015	-0.40648	H111	-0.30211	0.18304	-0.75240
C35	-0.75817	0.09861	-0.61791	H112	1.21767	0.68296	-0.74544
C36	-0.74864	0.09796	-0.37908	H113	1.31894	0.82096	-0.75240
C37	-0.75652	0.15535	-0.60228	H114	-1.16023	0.07108	-0.54428
C38	-0.64608	0.19976	-0.62860	H115	-0.99458	0.00074	-0.64904

C39	-0.53656	0.18837	-0.67121	H116	-0.65564	0.13545	-0.45831
C40	-0.54136	0.13202	-0.68741	H117	-0.65737	0.13557	-0.53879
C41	-0.65163	0.08775	-0.66102	H118	-0.99476	0.00071	-0.34800
C42	-0.64612	0.08686	-0.33585	H119	-0.84617	0.16570	-0.56765
C43	-0.52750	0.13058	-0.30953	H120	-0.64509	0.24554	-0.61532
C44	-0.50988	0.18663	-0.32593	H121	-0.45499	0.12227	-0.72224
C45	-0.61564	0.19830	-0.36863	H122	-0.65459	0.04228	-0.67485
C46	-0.73431	0.15445	-0.39487	H123	-0.65927	0.04164	-0.32185
N47	-0.42030	0.23459	-0.69723	H124	-0.44456	0.12079	-0.27459
N48	-0.38413	0.23225	-0.30005	H125	-0.60534	0.24379	-0.38222
C49	-0.27532	0.22496	-0.26048	H126	-0.82031	0.16507	-0.42959
C50	-0.15031	0.27349	-0.23627	H127	-0.27757	0.18062	-0.24468
C51	1.89372	0.95365	-0.59054	H128	-0.14458	0.31761	-0.25234
C52	1.89273	0.95374	-0.54460	H129	2.29397	0.98168	-0.52160
C53	2.00841	1.00200	-0.52160	H130	1.67418	0.86843	-0.53879
C54	1.77344	0.90735	-0.52104	H131	1.67377	0.86908	-0.45754
C55	1.77264	0.90742	-0.47603	H132	1.67134	0.96171	-0.67486
C56	1.89131	0.95383	-0.45244	H133	1.47164	0.88156	-0.72226
C57	2.00841	1.00200	-0.47542	H134	1.66242	0.75854	-0.61516
C58	1.89047	0.95385	-0.40648	H135	1.86298	0.83830	-0.56765
C59	1.77498	0.90539	-0.61791	H136	1.83710	0.83893	-0.42959
C60	1.76545	0.90604	-0.37908	H137	1.62159	0.76013	-0.38205
C61	1.66842	0.91624	-0.66102	H138	1.46161	0.88337	-0.2746
C62	1.55818	0.87198	-0.68741	H139	1.67600	0.96235	-0.32184
C63	1.55337	0.81563	-0.67121	H140	1.29436	0.82338	-0.24468
C64	1.66289	0.80424	-0.62860	H141	1.16138	0.68639	-0.25234
C65	1.77333	0.84865	-0.60228	H142	0.51063	0.50334	-0.14986
C66	1.75111	0.84955	-0.39487	H143	0.69359	0.37701	-0.01177
C67	1.63244	0.80570	-0.36863	H144	0.26450	0.36438	-0.03935
C68	1.52669	0.81737	-0.32593	H145	0.32324	0.62700	-0.01177
C69	1.54431	0.87342	-0.30953	H146	0.75233	0.63962	-0.03935
C70	1.66290	0.91713	-0.33585	H147	0.25207	0.45654	-0.17736
N71	1.43711	0.76941	-0.69723	H148	0.04368	0.37641	-0.22397
N72	1.40094	0.77175	-0.30005	H149	0.14447	0.25776	-0.11299
C73	1.29212	0.77904	-0.26048	H150	0.35050	0.33767	-0.06614
C74	1.16711	0.73051	-0.23627	H151	0.66627	0.66633	-0.06614
C75	0.42423	0.45165	-0.09134	H152	0.87282	0.74631	-0.11312
C76	0.44355	0.45095	-0.04547	H153	0.97286	0.62743	-0.22395
C77	0.50841	0.50200	-0.02280	H154	0.76466	0.54745	-0.17735

Table S8. Fractional atomic coordinates for the structural model 8 of PyG-COF in AA stacking.

The structural model 8 of PyG-COF in AA stacking							
a = 22.86 Å, b = 30.40 Å, c = 3.64 Å, $\alpha = \beta = 90°$, $\gamma = 89.79°$							
C1	-7.13681	2.34433	-0.92718	C78	-8.28083	2.7646	-0.73986

C2	-7.83759	2.64642	-0.92718	N79	-8.37143	2.74253	-0.70221
C3	-7.93119	2.61904	-0.88741	C80	-7.41865	2.46617	-0.00826
C4	-8.01714	2.65191	-0.85008	C81	-7.35078	2.43708	-0.04865
C5	-8.01336	2.71322	-0.85188	C82	-7.21977	2.37863	-0.04868
C6	-7.92314	2.74092	-0.89136	C83	-7.55563	2.52459	-0.00826
C7	-7.83697	2.70787	-0.92864	C84	-7.62342	2.55369	-0.04865
C8	-7.13746	2.28288	-0.92864	C85	-7.55258	2.52392	-0.08792
C9	-7.05137	2.24984	-0.89136	C86	-7.42151	2.46685	-0.08792
C10	-6.96113	2.27753	-0.85188	C87	-7.7544	2.61213	-0.04868
C11	-6.95732	2.33884	-0.85008	C88	-7.13668	2.34434	-0.08934
C12	-7.04326	2.37172	-0.88740	C89	-7.62349	2.55368	-0.96787
C13	-6.25464	2.11212	-0.54868	C90	-7.7545	2.61213	-0.96783
C14	-6.12352	2.05368	-0.54865	C91	-7.35085	2.43707	-0.96786
C15	-6.05561	2.02459	-0.50826	C92	-7.42169	2.46684	-0.92859
C16	-6.12349	2.05369	-0.46786	C93	-7.55276	2.52391	-0.92859
C17	-6.25458	2.11212	-0.46783	C94	-7.21986	2.37863	-0.96783
C18	-6.31394	2.13973	-0.50826	C95	0.83945	-0.64898	-1.00826
C19	-6.05273	2.02392	-0.58792	C96	0.18628	-0.36026	-1.00826
C20	-6.05261	2.02392	-0.42859	H97	-7.93778	2.56927	-0.88528
C21	-6.3378	2.14641	-0.58934	H98	-8.09071	2.62894	-0.81800
C22	-6.33771	2.14642	-0.42718	H99	-7.91958	2.79071	-0.89327
C23	-6.33732	2.20786	-0.58788	H100	-7.76548	2.73142	-0.96055
C24	-6.42353	2.24090	-0.62516	H101	-7.20891	2.25934	-0.96056
C25	-6.51372	2.21320	-0.66464	H102	-7.05457	2.20003	-0.89307
C26	-6.51736	2.15189	-0.66643	H103	-6.88386	2.36197	-0.81806
C27	-6.43132	2.11902	-0.62911	H104	-7.03674	2.42149	-0.88527
C28	-6.43121	2.11903	-0.38740	H105	-6.41538	2.18694	-0.50726
C29	-6.51720	2.15190	-0.35008	H106	-6.10267	2.04651	-0.62083
C30	-6.51352	2.21321	-0.35188	H107	-6.31668	2.02447	-0.40848
C31	-6.42335	2.24091	-0.39136	H108	-5.83638	2.04861	-0.40893
C32	-6.33719	2.20787	-0.42864	H109	-6.26591	2.23141	-0.55597
N33	-6.87191	2.24250	-0.81430	H110	-6.42047	2.29071	-0.62344
C34	-6.78126	2.26457	-0.77665	H111	-6.59077	2.12874	-0.69845
C35	-6.69365	2.22616	-0.73986	H112	-6.43775	2.06925	-0.63124
N36	-6.60302	2.24823	-0.70222	H113	-6.43765	2.06926	-0.38527
C37	-6.78102	2.26458	-0.23986	H114	-6.59075	2.12893	-0.31799
C38	-6.69342	2.22617	-0.27665	H115	-6.41983	2.29070	-0.39327
N39	-6.60279	2.24824	-0.31430	H116	-6.26579	2.23142	-0.46056
C40	-7.83742	2.64643	-0.08934	H117	-6.76999	2.31406	-0.77229
C41	-7.04311	2.37173	-0.12911	H118	-6.70496	2.17668	-0.74424
C42	-6.95712	2.33885	-0.16643	H119	-6.76974	2.31407	-0.24422
C43	-6.96090	2.27754	-0.16464	H120	-6.70472	2.17669	-0.27227
C44	-7.05116	2.24985	-0.12516	H121	-7.03660	2.42150	-0.13124
C45	-7.13730	2.28289	-0.08788	H122	-6.88347	2.36181	-0.19851
C46	-7.83669	2.70788	-0.08788	H123	-7.05478	2.20006	-0.12325

C47	-7.92279	2.74093	-0.12516	H124	-7.20941	2.26005	-0.05570
C48	-8.01309	2.71324	-0.16464	H125	-7.76517	2.73142	-0.05597
C49	-8.01694	2.65192	-0.16643	H126	-7.91954	2.79074	-0.12344
C50	-7.93105	2.61905	-0.12911	H127	-8.09040	2.62878	-0.19845
N51	-6.87166	2.24251	-0.20222	H128	-7.93769	2.56928	-0.13124
C52	-8.71951	2.87865	-0.46783	H129	-8.55877	2.80383	-0.50926
C53	-8.85062	2.93709	-0.46786	H130	-8.65734	2.96631	-0.40848
C54	-8.91853	2.96618	-0.50826	H131	-9.13764	2.94217	-0.40893
C55	-8.85068	2.93709	-0.54865	H132	-8.87164	2.94426	-0.62083
C56	-8.71957	2.87865	-0.54868	H133	-8.70836	2.75937	-0.46056
C57	-8.66021	2.85104	-0.50826	H134	-8.55389	2.70006	-0.39308
C58	-8.92144	2.96686	-0.42859	H135	-8.38337	2.86202	-0.31806
C59	-8.92153	2.96685	-0.58792	H136	-8.53630	2.92152	-0.38528
C60	-8.63637	2.84436	-0.42717	H137	-8.53647	2.92151	-0.63124
C61	-8.63645	2.84435	-0.58934	H138	-8.38344	2.86183	-0.69852
C62	-8.63693	2.78291	-0.42864	H139	-8.55434	2.70007	-0.62325
C63	-8.55076	2.74987	-0.39136	H140	-8.70848	2.75936	-0.55597
C64	-8.46053	2.77757	-0.35188	H141	-8.20424	2.67671	-0.24423
C65	-8.4568	2.83888	-0.35008	H142	-8.26924	2.81409	-0.27226
C66	-8.54281	2.87175	-0.38741	H143	-8.20443	2.67669	-0.77229
C67	-8.54295	2.87174	-0.62911	H144	-8.26956	2.81408	-0.74425
C68	-8.45699	2.83887	-0.66643	H145	-7.84874	2.50731	-0.00827
C69	-8.46068	2.77756	-0.66464	H146	-7.60238	2.54651	-0.12083
C70	-8.55084	2.74986	-0.62516	H147	-7.37162	2.44427	-0.12083
C71	-8.63702	2.78291	-0.58788	H148	-7.91752	2.53680	-0.9678
N72	-8.10230	2.74827	-0.20222	H149	-7.46021	2.62889	-0.96738
C73	-8.19297	2.72620	-0.23987	H150	-7.37189	2.44425	-0.89568
C74	-8.28057	2.76461	-0.27665	H151	-7.60266	2.54650	-0.89568
N75	-8.37125	2.74254	-0.31430	H152	0.94079	-0.69619	-1.00726
N76	-8.10260	2.74825	-0.81430	H153	-0.10962	-0.34389	-1.00827
C77	-8.19321	2.72618	-0.77665	H154	0.36983	-0.32013	-1.00570

Table S9. The detailed information of N 1*s* XPS spectra of different COFs.

Sample	Functional group	Position (eV)	Area	FWHM (eV)
PyG-COF	Imine N	399.5	1497.39	2.03
PyG-Im-COF	Imine N	399.5	1652.47	1.74
	Imidazolium N	401.8	242.63	1.75

Table S10. The HER performance comparison of PyG-Im-COF with other nitrogen-containing heterocycle-based COFs.

COFs	Photoactive units	Pt contents (wt%)	Electron donors	Irradiation condition	HER ($\mu mol\ g^{-1}\ h^{-1}$)	AQY	Ref.

BT-TAPT-COF	benzothiadiazole	8	AC	λ > 420 nm	919	0.19% (410 nm)	[2]
Py-ClTP-BTCOF	dichlorobenzo[c] thiadiazole	5	AC	λ > 420 nm	8875	8.45% (420 nm)	[3]
PyTA-BC-Ph COF	9,9'-bicarbazole	3.7	AC	λ > 420 nm	2763	1.83% (420 nm)	[4]
PyTz-COF	thiazolo[5,4-d] thiazole	3	AC	AM 1.5	2072	-	[5]
PETZ-COF	thiazolo[5,4-d] thiazole	3	AC	λ > 420 nm	7324	3.64% (520 nm)	[6]
BtCOF150	benzothiadiazole	1	TEOA	λ > 400 nm	750	0.2% (420 nm)	[7]
N1-COF	pyridyl	1.7	TEOA	λ > 420 nm	90	0.08% (450 nm)	[8]
N2-COF	pyrimidyl	0.94	TEOA	λ > 420 nm	438	0.19% (450 nm)	[8]
N3-COF	triazine	0.68	TEOA	λ > 420 nm	1703	0.44% (450 nm)	[8]
PyG-Im-COF	Imidazolium	0.57	AC	λ > 420 nm	1866	0.39% (420 nm)	**This work**

Section S4. *References*

(1) P. J. Rayner, P. Norcott, K. M. Appleby, W. Iali, R. O. John, S. J. Hart, A. C. Whitwood and S. B. Duckett, *Nat. Commun.*, 2018, **9**, 4251.

(2) G. B. Wang, S. Li, C. X. Yan, Q. Q. Lin, F. C. Zhu, Y. Geng and Y. B. Dong, *Chem. Commun.*, 2020, **56**, 12612-12615.

(3) W. B. Chen, L. Wang, D. Z. Mo, F. He, Z. L. Wen, X. J. Wu, H. X. Xu and L. Chen, *Angew. Chem., Int. Ed.*, 2020, **59**, 16902-16909.

(4) A. F. M. El-Mahdy, A. M. Elewa, S.-W. Huang, H.-H. Chou and S.-W. Kuo, *Adv. Opt. Mater.*, 2020, **8,** 2000641.

(5) W. Q. Li, X. F. Huang, T. W. Zeng, Y. H. A. Liu, W. B. Hu, H. Yang, Y. B. Zhang and K. Wen, *Angew. Chem., Int. Ed.*, 2021, **60**, 1869-1874.

(6) H. P. Yu, J. Z. Zhang, X. R. Yan, C. G. Wu, X. R. Zhu, B. W. Li, T. F. Li, Q. Q. Guo, J. F. Gao, M. J. Hu and J. Yang, *J. Mater. Chem. A*, 2022, **10**, 11010-11018.

(7) S. Ghosh, A. Nakada, M. A. Springer, T. Kawaguchi, K. Suzuki, H. Kaji, I. Baburin, A. Kuc, T. Heine, H. Suzuki, R. Abe and S. Seki, *J. Am. Chem. Soc.*, 2020, **142**, 9752-9762.

(8) V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld and B. V. Lotsch, *Nat. Commun.*, 2015, **6**, 8508.