Supplementary Information (SI) for Nanoscale.

Experimental Section

Materials:

1,2,4,5-Benzenetetramine tetrahydrochloride (TABH, 97%) was purchased from Bidepharm Ltd, Shanghai, China. Anhydrous ferric trichloride, ($FeCl_3$, 99%), Pyromellitic dianhydride (PMDA, 99%), p-Phenylenediamine (PDA, 99.9%) and Cobaltous nitrate ($Co(NO_3)_2$) were purchased from Beijing InnoChem Science & Technology Co., Ltd. polyphosphoric acid (PPA, 85%) were purchased from Shanghai Macklin Biochemical Co., Ltd.

Synthesis of polymers:

Lad-CP: The sample ladder polymer (Lad-CP) was synthesized by condensation between 1,2,4,5-Benzenetetramine tetrahydrochloride (TABH) and Pyromellitic dianhydride (PMDA) in polyphosphoric acid (PPA). TABH (0.5g, 1.76mmol) and PPA (45g, 85%P_2O_5 assay) were charged in reaction flask equipped with a high-torque mechanical stirrer under argon atmosphere. The reaction temperature was stepwise increased to 60°C and stirred for 12 hours to completely remove HCl in the TABH. After complete removal of the HCl gas, PMDA (0.384g, 1.76mmol) was added. The reaction was continued to be stirred at this temperature for 12 hours. Then, the reaction temperature was gradually increased to 180°C for 24h. After cool to room temperature, water, methanol and acetone were added to the reaction mixture, yellow chunk was collected and Soxhlet extracted.

Lin-CP: The sample linear polymer (Lin-CP) was synthesized by condensation between PMDA and p-Phenylenediamine (PDA). 0.327 g (1.5 mmol) of PDMA were placed in a 3-neck-flask under inert atmosphere, equipped with a reflux condenser and dissolved in 15mL of deionized water (previously degassed with N2). The solution was heated to 80 °C and 0.162 g freshly resublimated PDA (1.5 mmol) were added under stirring. The white salt precipitated immediately, and the dispersion was further stirred for 2 h at 80 °C. The freshly prepared salt dispersion was transferred to an autoclave (V = 45 mL), equipped with a Teflon liner. The autoclave was placed in an oven at different temperatures 260 °C and kept there for 6h. At the end of the reaction, the autoclave was cooled to room temperature. And solid product washed several times with distilled water, methanol and acetone. And the product was collected and Soxhlet extracted.

Characterization:

Transmission electron microscopy (TEM) was operated by a Tecnai20 FEG microscope and Titan G2 60-300 with an image corrector. The Fourier transform infrared (FTIR) spectra were recorded on a BioRad FTS 6000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo ESCALAB250 instrument with a monochromatized Al Kα line source (200 W). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were performed on the Varian Cary 500 Scan UV-visible system. The electron paramagnetic resonance (EPR) measurements were carried out on a Bruker Model A300 spectrometer. Nitrogen adsorption-desorption isotherms were performed at 77 K using Micromeritics ASAP 3020 equipment. The solid-state ^{13}C NMR experiments were performed on a Bruker Advance III 500 spectrometer. Photocurrent performance was conducted with a BAS Epsilon Electrochemical System in a conventional three-electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl (3 M KCl) electrode as the reference electrode. The working electrode was prepared on indium-tin-oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of DMF by sonication to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin.

Photocatalytic O_2 evolution test:

Photocatalytic oxygen evolution arrays were performed in a Pyrex top-irradiation reaction vessel linked to a glass-closed gas system. O_2 production was carried out by dispersing 10 mg of photocatalyst powder in an aqueous solution (100 mL) containing 0.2g La_2O_3, 0.17g $AgNO_3$. A certain amount of $Co(NO_3)_2$ was added into the solution system to deposit 3 wt% of Co onto the photocatalyst by photodeposition. The temperature of the reaction solution was kept at 12 °C by a flow of cooling water. The generated gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with Argon as the carrier gas.

AQY measurement for O_2 evolution:

The apparent quantum yield (AQY) for the O_2 evolution was determined by the 420 nm LED monochromatic lamp with a 420 nm semiconductor laser. The irradiation area was 1 cm^2. The total intensity irradiation was measured by averaging 40 points in the irradiation area. The AQY was calculated as:

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{4MN_A hc}{SPt\lambda} \times 100\%$$

where N_e is the number of reaction electrons, N_p is the number of incident photons, M is the amount of O_2 molecules (mol), N_A is Avogadro's constant (6.022×10^{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 the irradiation (W cm^{-2}), t is the photoreaction time (s), and λ is the wavelength of the monochromatic light (m).

Details of theoretical calculations:

All calculations were carried out using density functional theory (DFT) by employing the Vienna Ab-initio Simulation Package (VASP) code.[1] The structural information of Lin-CP and Lad-CP was simulated by Materials Studio software. Nuclei and core electrons were described by the projector augmented wave (PAW) potentials. The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was employed, combined with Grimme's DFT-D3 correction. A Monkhorst-Pack mesh of 7×7×1 k-points was used in the 2D Brillouin zone for geometry optimizations and electronic structure calculations. The cut-off energy of the plane-wave expansion was set to 550 eV, and the convergence thresholds of the energy change and the maximum force were set to 10-5 eV and 0.01 eV/Å, respectively. A vacuum space was set to 20 Å to avoid the interactions between neighboring layers. Due to that, the PBE functional underestimates the band gaps of semiconductors; all electronic structures were further calculated using the HSE06 hybrid functional. The electrostatic potential (ESP) and dipole moment of Lin-CP and Lad-CP were calculated on the Gaussian 09W software package. Quantitative molecular surface analysis was investigated by Multiwfn (main function 12).[2]

Results and Discussion

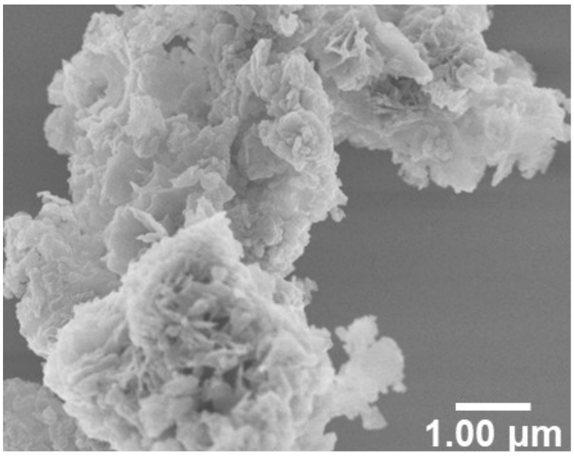

Figure S1. SEM image of Lin-CP

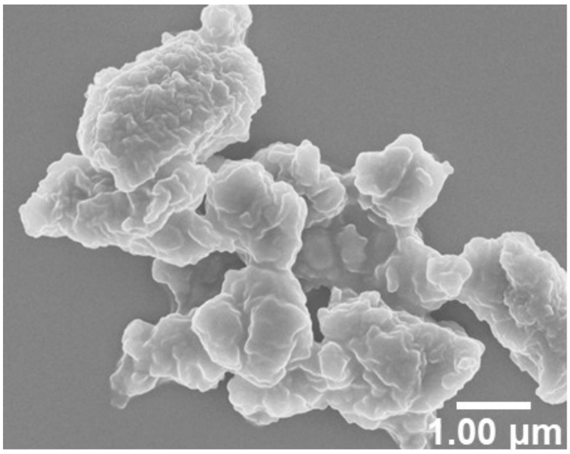

Figure S2. SEM image of Lad-CP

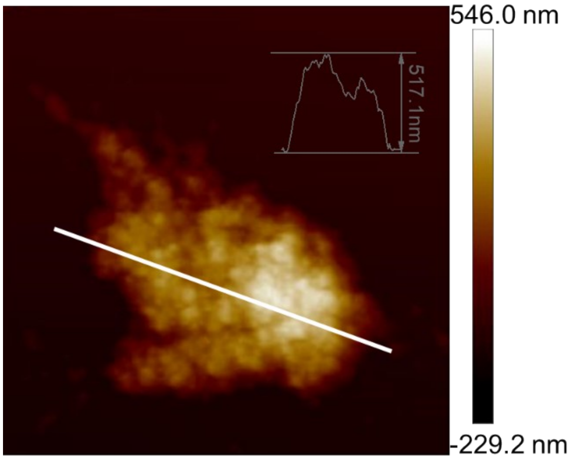

Figure S3. AFM image of Lin-CP

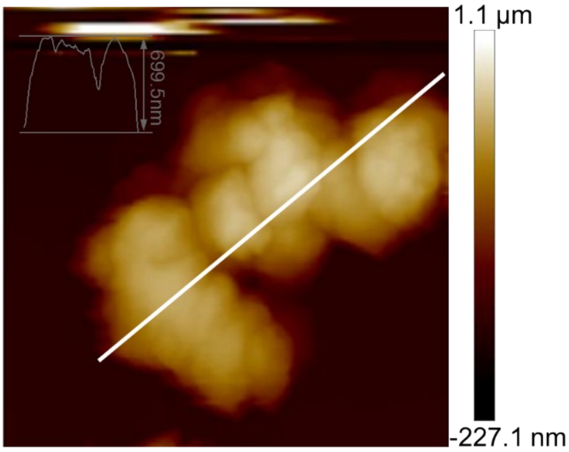

Figure S4. AFM image of Lad-CP

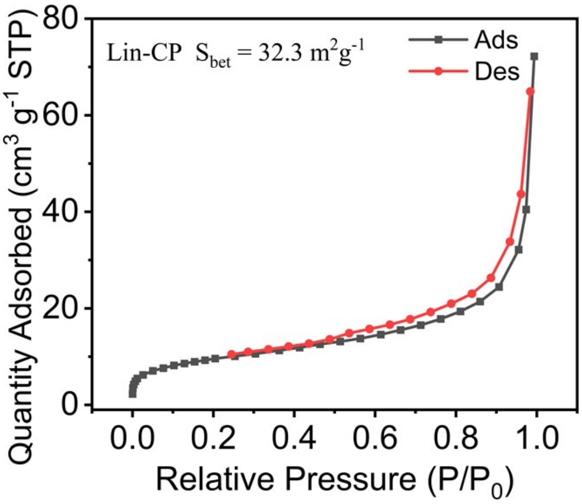

Figure S5. Nitrogen sorption isotherm for Lin-CP collected at 77 K.

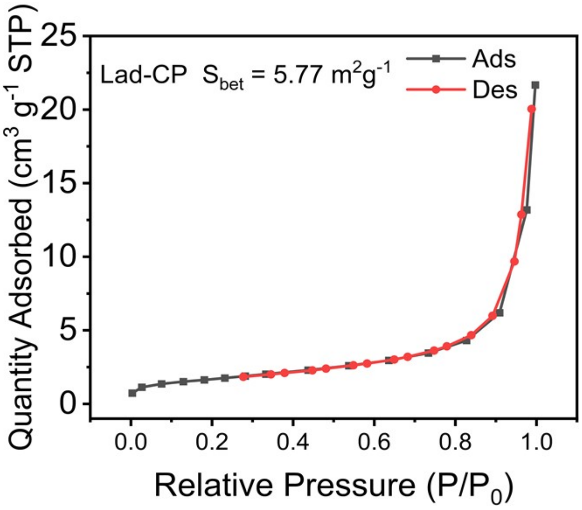

Figure S6. Nitrogen sorption isotherm for Lad-CP collected at 77 K.

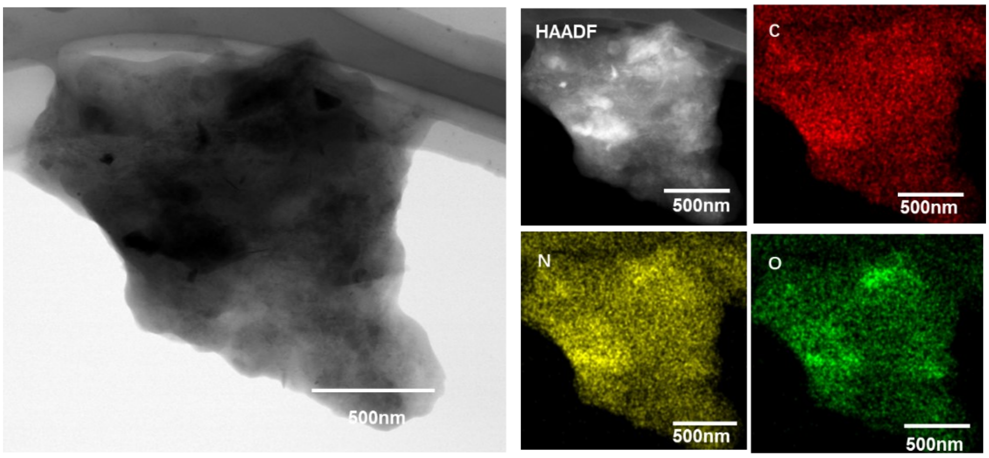

Figure S7. TEM image of Lin-CP with elemental maps for C, N and O.

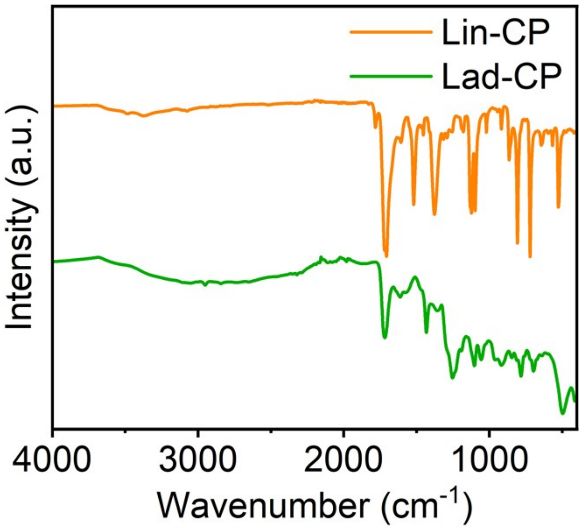

Figure S8. FT-IR spectra of Lin-CP and Lad-CP.

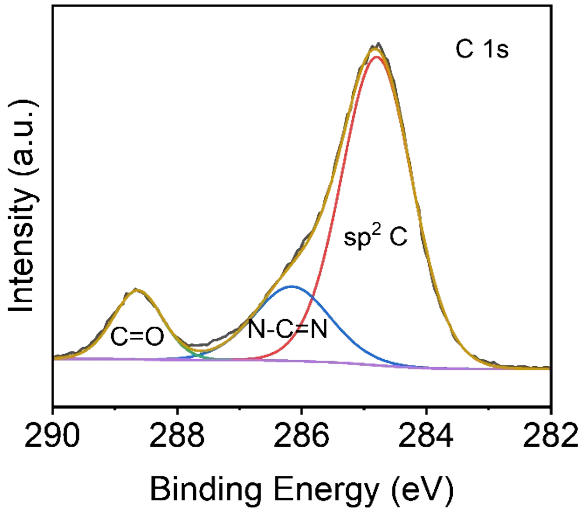

Figure S9. XPS spectra of Lad-CP: C 1s

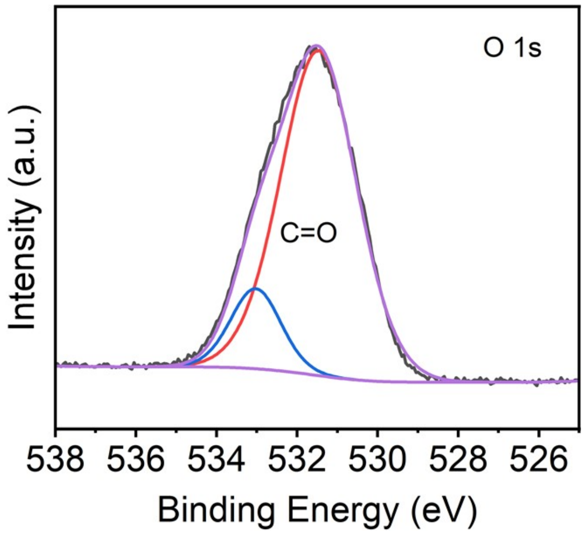

Figure S10. XPS spectra of Lad-CP: O 1s.

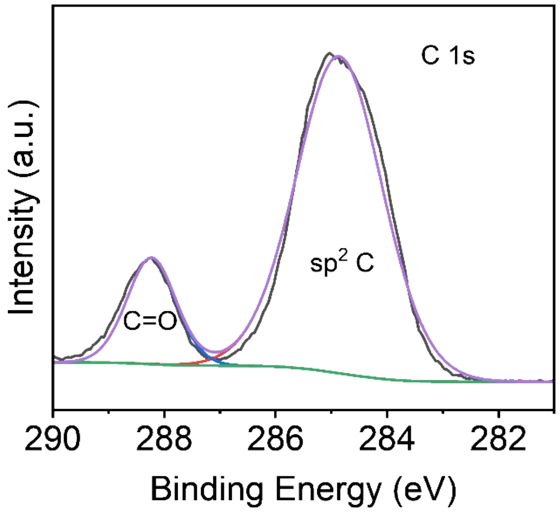

Figure S11. XPS spectra of Lin-CP: C 1s.

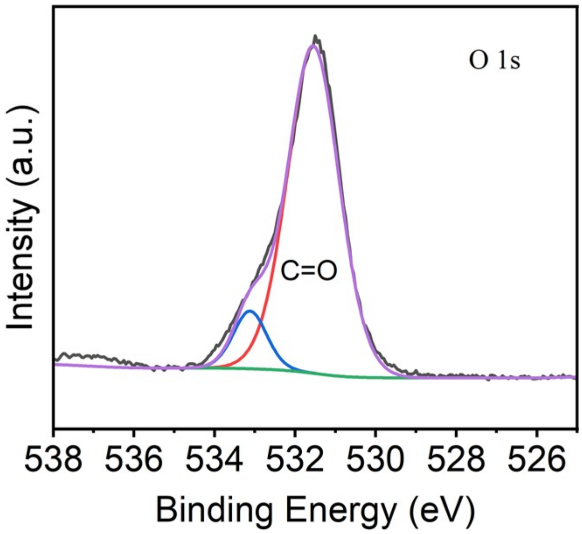

Figure S12. XPS spectra of Lin-CP: O 1s.

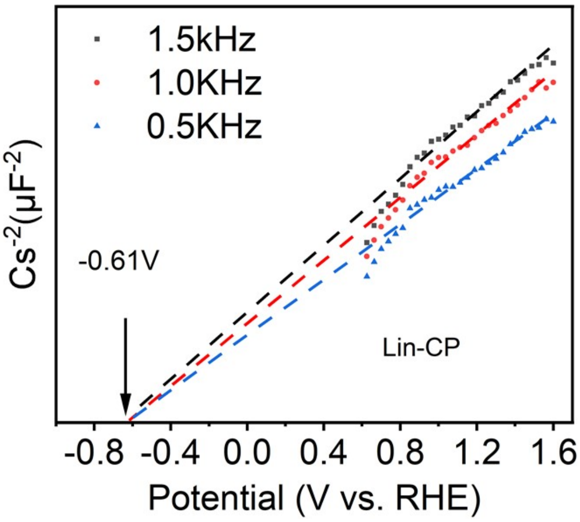

Figure S13. Mott-Schottky plots of Lin-CP

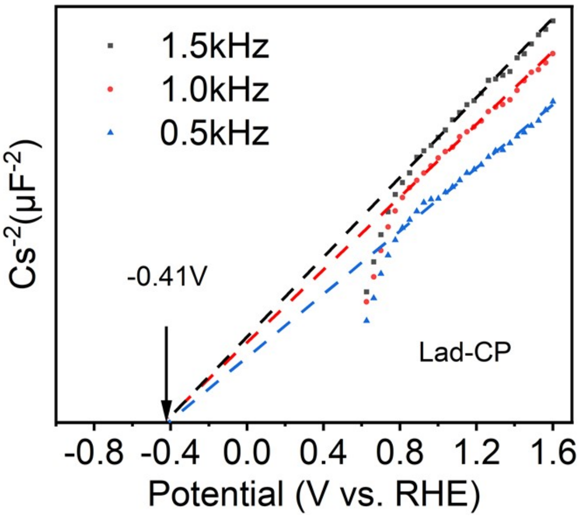

Figure S14. Mott-Schottky plots of Lad-CP

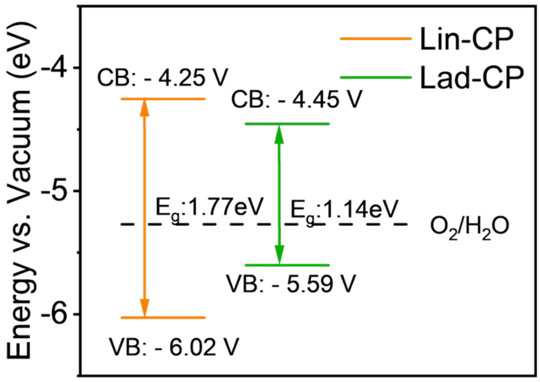

Figure S15. Theoretical band structure diagram for Lad-CP and Lin-CP (Potential,pH=7)

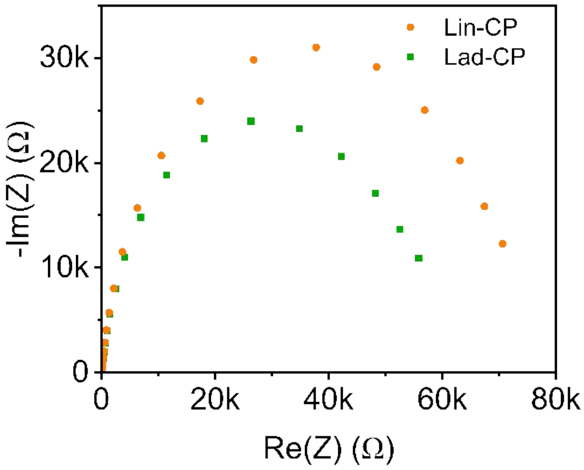

Figure S16. EIS spectra of Lad-CP and Lin-CP.

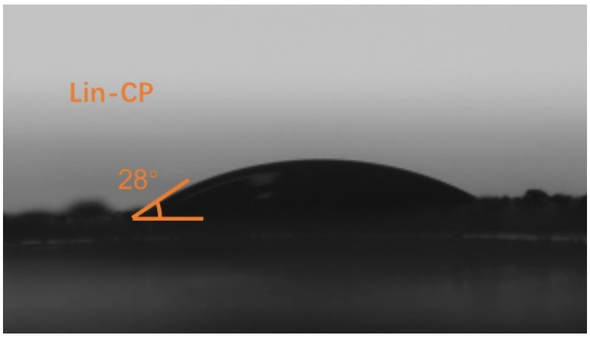

Figure S17. Water contact angles of Lin-CP

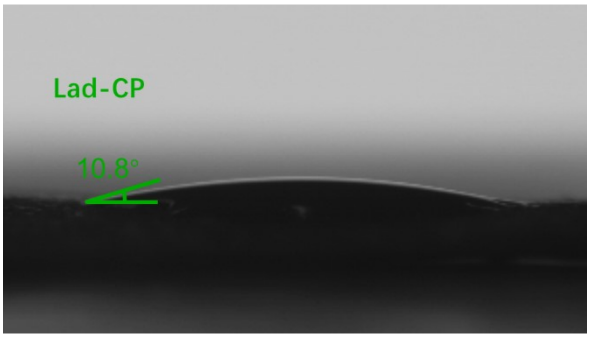

Figure S18. Water contact angles of Lad-CP

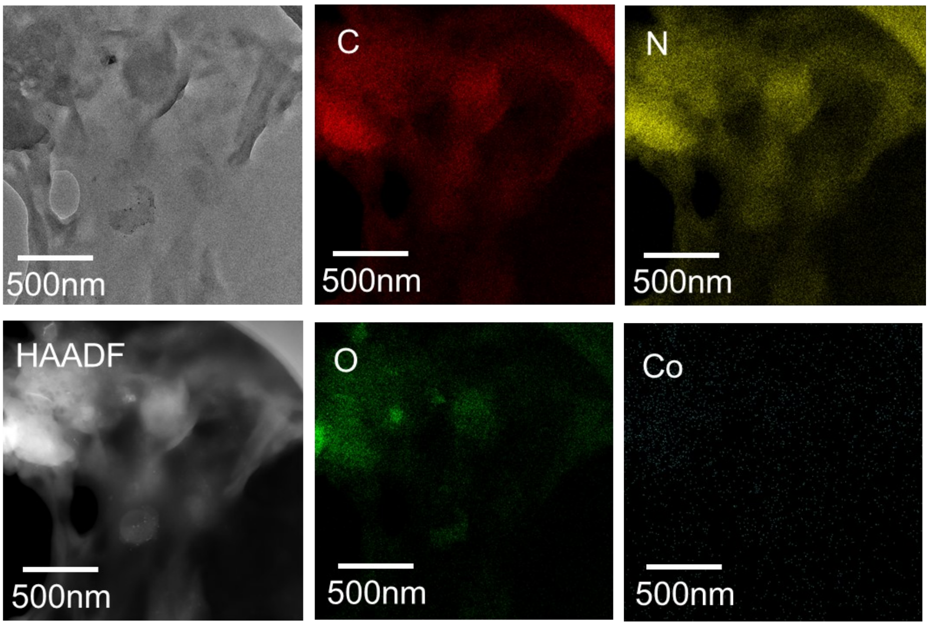

Figure S19. Lad-CP with 1% cobalt addition

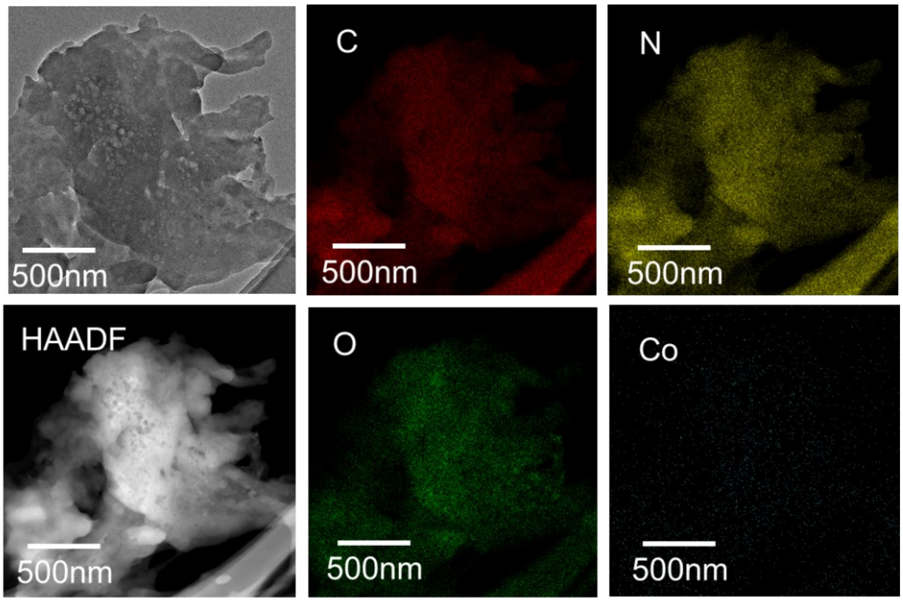

Figure S20. Lad-CP with 3% cobalt addition

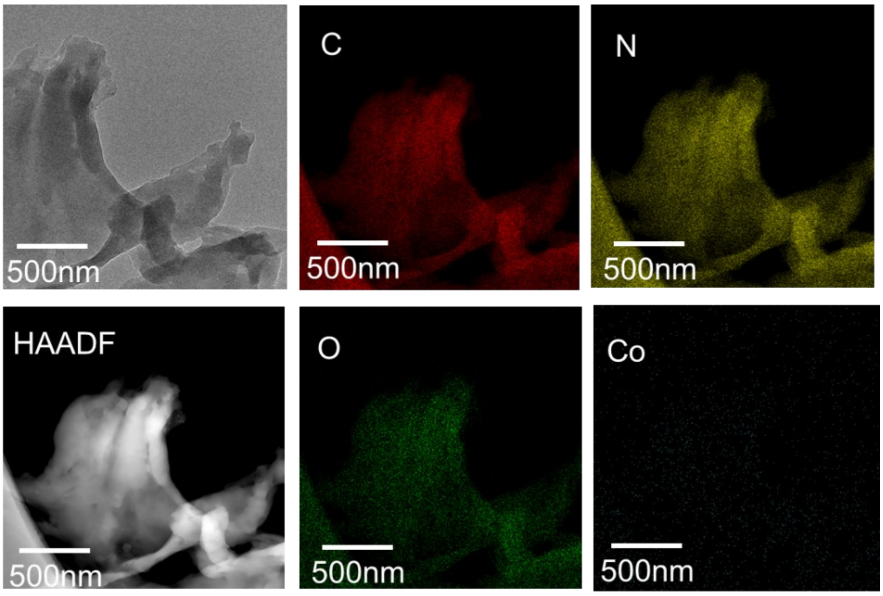

Figure S21. Lad-CP with 4% cobalt addition

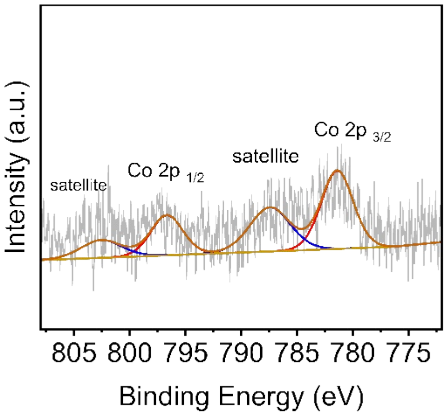

Figure S22. The XPS spectra of Co loading

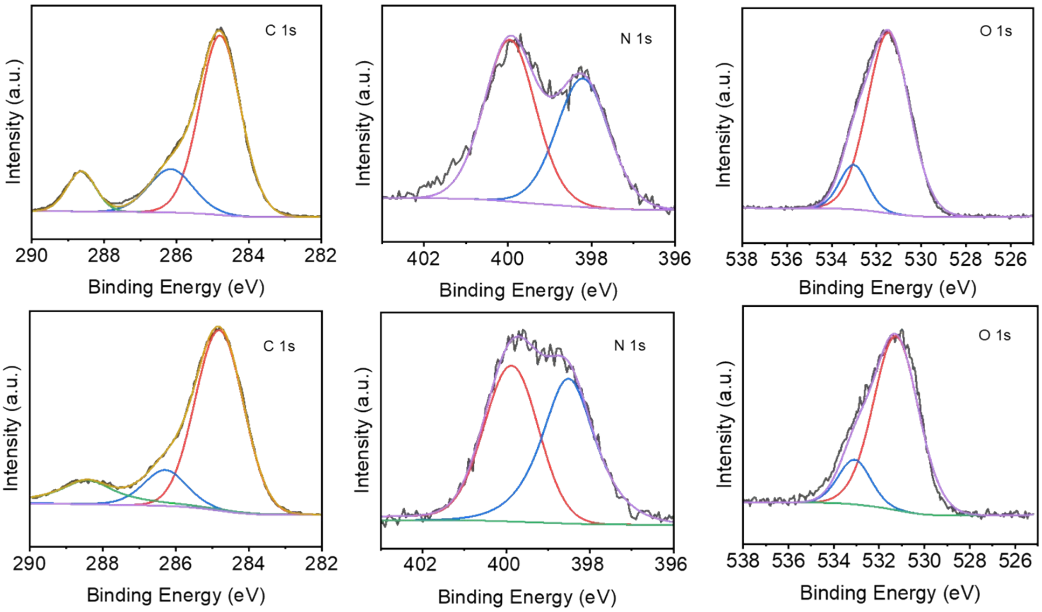

Figure S23. XPS spectra of Lad-CP before (up) and after (down) experiment.

Table S1. OERs of reported conjugated polymers under visible light irradiation.

Photocatalyst	AQY	Light irradiation wavelength (nm)	Reference
Lad-CP	3.19%	420	This work
$CoCl_2$-TpBpy	1.34%	425	*Small* 2024, **20**, 2401168
Bpy→CoTPP-DMTP-COF	1.03%	420	*Angew. Chem. Int. Ed.* 2024, **63**, e202416771
Bpy-CTF	0.56%	420	*Catal. Sci. Technol.* 2022, **12**, 5442-5452.
PTPP	2.11%	420	*Chinese J. Chem.* 2021, **39**, 1079-1084
PQL	0.63%	420	*Chinese J. Chem.* 2021, **39**, 1079-1084
BpCo-COF-1	0.46%	420	*Appl. Catal., B*, 2020, **262**, 118271
Urea-PDI	2.11%	420	*Adv. Mater.* 2020, **32**, 1907746.

Table S2. Co Load Measurement by ICP-OES

Cobalt addition	Cobalt loading
1%	0.3%
3%	1%
4%	2%

Table S3. The Cartesian coordinates for the optimized geometries of two simulated fragmental structures of Lin-CP and Lad-CP.

Lin-CP:
Lattice type P
Space group name P 1
Space group number 1
Setting number 1
Lattice parameters:
a: 12.41849 Å b: 16.04780 Å c: 19.98515 Å alpha: 90.0849° beta: 88.0678° gamma: 88.4121°

Atom	x	y	z
C	0.0378	0.5505	0.48228
C	0.09806	0.4825	0.45561
C	0.21008	0.48248	0.45561
C	0.26261	0.55049	0.48225
C	0.20234	0.61851	0.50891
C	0.09032	0.6185	0.50893
C	0.44374	0.47909	0.49463
C	0.55674	0.50784	0.4896

C	0.55448	0.59317	0.47492
C	0.43995	0.62191	0.46988
C	0.65253	0.46215	0.49752
C	0.74589	0.50786	0.48969
C	0.74364	0.59317	0.47487
C	0.64785	0.63886	0.46701
C	0.86043	0.4792	0.49496
C	0.8567	0.62184	0.46963
N	0.3771	0.55049	0.48225
N	0.9233	0.55052	0.48229
O	0.40541	0.69188	0.45739
O	0.41287	0.40912	0.50715
O	0.88767	0.69168	0.45673
O	0.89501	0.40937	0.50789
H	0.05759	0.42936	0.43514
H	0.25653	0.42926	0.43519
H	0.24279	0.67171	0.52933
H	0.04384	0.67163	0.52941
H	0.65434	0.39566	0.50887
H	0.64612	0.70535	0.45566

Lad-CP:
Lattice type P
Space group name P 1
Space group number 1
Setting number 1
Lattice parameters:
a: 11.85364 Å b: 12.48554 Å c: 19.33738 Å alpha: 89.3961° beta: 89.2436° gamma: 88.6032°

Atom	x	y	z
C	0.06776	0.45775	0.50558
C	0.02625	0.64181	0.50836
C	0.24741	0.43473	0.50525
C	0.22843	0.54905	0.50696
C	0.35681	0.39002	0.50458
C	0.44167	0.46455	0.50570
C	0.42270	0.57888	0.50741
C	0.31329	0.62358	0.50807
C	0.60234	0.55588	0.50707
C	0.64386	0.37181	0.50433
C	0.75087	0.43342	0.50525
C	0.72452	0.54492	0.50690
C	0.86103	0.39276	0.50463
C	0.94558	0.46871	0.50575
C	0.91923	0.58021	0.50742

C	0.80907	0.62088	0.50802
N	0.11161	0.56075	0.50712
N	0.14535	0.38107	0.50444
N	0.55850	0.45287	0.50553
N	0.52475	0.63255	0.50821
O	0.04035	0.73812	0.50983
O	0.62976	0.27551	0.50291
H	0.37322	0.30388	0.50329
H	0.29689	0.70973	0.50935
H	0.87971	0.30682	0.50335
H	0.79040	0.70682	0.50929

References

[1] G. Kresse, J. Furthmüller, *Comput. Mater. Sci*. **1996**, *6*, 15.

[2] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery,Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M.Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian,J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R.Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg,V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K.Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G.Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A.Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople,Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford CT, 2004.