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Dynamic structural twist in metal-organic frameworks enhances solar overall water splitting

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Photocatalytic overall water splitting holds great promise for solar-to-hydrogen conversion. Maintaining charge separation is a major challenge but is key to unlocking this potential. Here we discovered a metalorganic framework (MOF) that shows suppressed charge recombination. This MOF features electronically insulated Zn²⁺ nodes and two chemically equivalent, yet crystallographically independent, linkers. These linkers behave as an electron donor-acceptor pair with non-overlapping band edges. Upon photoexcitation, the MOF undergoes a dynamic excited-state structural twist, inducing orbital rearrangements that forbid radiative relaxation and thereby promote a long-lived charge-separated state. As a result, the MOF achieves visible-light photocatalytic overall water splitting, in the presence of co-catalysts, with an apparent quantum efficiency of $3.09 \pm 0.32\%$ at 365 nm and shows little activity loss in 100 h of consecutive runs. Furthermore, the dynamic excited-state structural twist is also successfully extended to other photocatalysts. This strategy for suppressing charge recombination will be applicable to diverse photochemical processes beyond overall water splitting.

The conversion of solar energy into hydrogen fuel has garnered considerable attention as an emerging technology for clean energy production¹. Although some photocatalysts have been developed to catalyse the individual half-reactions involved in splitting H₂O with sacrificial reagents²⁻⁶, attaining overall water splitting (OWS), particularly with one-step photoexcitation under visible-light irradiation, remains an elusive yet highly desirable target⁶⁻¹⁴. The proton-coupled electron transfer process involved in photocatalytic OWS often leads to the recombination of photogenerated carriers before protons can migrate to the catalytic

sites, stalling the reaction. Accordingly, rapid charge recombination is a major bottleneck for photocatalytic OWS^{1,6}. Current approaches to suppressing charge recombination generally involve regulating the ground-state structure of catalysts; however, biological insight suggests that an alternative strategy involving excited states may be fruitful.

Biological photosynthesis illustrates the effective leveraging of structural flexibility for charge separation. In natural photosynthesis, photoexcited electrons migrate to catalytic sites via cofactors. Cofactors create a localized charge distribution in the excited photosynthetic

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Fig. 1 | Chemically segregated system construction and structural characterization. a, Possible constructions of chemically segregated donor and acceptor systems for different types of photocatalysts. b, The $[Zn_sX_4(L)_s]$ SBU in

the CFA-Zn structure viewed along the *c* axis with X and hydrogen atoms omitted for clarity. **c**, SEM image of CFA-Zn. Inset: simulated exposed facets of the MOF crystal.

protein¹⁵, triggering a conformational change that stabilizes spatial charge separation and extends electron lifetime¹⁶. Natural photosynthesis has inspired efforts to arrange electron-donor (light-harvesting) and electron-acceptor units in a chemically segregated state, with an electronic insulator between them to prevent electron cloud overlap. This will create a highly localized charge distribution in the excited state, which then brings about a structural distortion to relax the system energy. Such a structural rearrangement, in turn, causes marked changes in the catalyst's potential energy surface that block the relaxation pathway from the excited state to the original ground state, in which radiative relaxation is forbidden¹⁷, thereby prolonging the lifetime of the charge-separated state.

These considerations highlight the advantages afforded by a photocatalyst's structural dynamism and by the separation of its donor and acceptor units with an electronic insulator, enabling structural distortion in the excited state for suppressed charge recombination. Unfortunately, for common heterogeneous photocatalysts, the rigidity of inorganic semiconductors and the orbital overlap in polymeric organic semiconductors with delocalized bonds have curtailed the realization of suppressed radiative relaxation through an excited-state structural distortion¹⁸. In contrast, metal–organic frameworks (MOFs), which are constructed from metal ions/clusters and organic linkers via coordination bonds and feature flexible and customizable structures^{19–26}, are ideal for the design of these photocatalysts. Moreover, closed-shell metal ions/nodes can be used to chemically segregate the organic linkers of MOFs in a manner that stabilizes charge-separated states for photocatalytic OWS (Fig. 1a and Supplementary Discussion 1).

In this work, an MOF with closed-shell Zn²⁺ nodes, denoted as CFA-Zn (ref. 27), has been discovered to accomplish visible-light photocatalytic OWS by one-step photoexcitation. Unlike the high-symmetry MOFs with redox-active metal nodes that are commonly investigated in photocatalysis, CFA-Zn features a highly asymmetric structure and Zn²⁺ nodes with d¹⁰ configuration. Such an asymmetric structure enables two chemically equivalent yet crystallographically independent linkers to contain utterly different orbitals, behaving as an electron donor-acceptor pair. The Zn²⁺ nodes act as electronic insulators that chemically segregate the two linkers. Upon photoexcitation, the catalyst's flexibility facilitates a twisting motion that forbids radiative relaxation and thereby suppresses charge recombination. In addition, the preferential deposition of platinum co-catalysts on the MOF (001) facet provides ideal platinum sites and greatly boosts photocatalytic activity. As a result, the CFA-Zn system achieves visible-light OWS performance, showcasing an apparent quantum efficiency (AQE) of $3.09 \pm 0.32\%$ (365 nm) with co-catalysts. This photocatalytic activity is maintained with little degradation during ten runs amounting to 100 h. This work reveals that dynamic structural twist of photocatalysts in the excited state opens an avenue to forbidden radiative relaxation for suppressed charge recombination and enhanced photocatalysis.

Results and discussion

Synthesis and structural analysis

CFA-Zn, formulated as $Zn_5(OAc)_4(bibta)_3$ (OAc = acetate, bibta = 5,5'-bibenzo[*d*][1,2,3]triazole), was synthesized by a facile solvothermal method (Supplementary Figs. 1–3). Over 20 g of CFA-Zn can be harvested in high yield (94.5%) from a one-pot scaled-up synthesis; the resulting MOF shows very high crystallinity and largely retains the Brunauer–Emmett–Teller surface area (Supplementary Figs. 3–5). The secondary building unit (SBU) of CFA-Zn is a Kuratowski-type consisting of [Zn₅X₄(triazolate)₆] (X = Cl⁻ or acetate) in *T_d* point group symmetry (Supplementary Fig. 6). Each SBU is connected by six skewed bibta^{2–} linkers that are divided into two types of crystallographically independent linkers (Fig. 1b). Theoretical simulations²⁷ and scanning electron microscopy (SEM) results show that different crystal facets on the MOF particle are exposed (Fig. 1c).



Fig. 2 | **Analysis of orbitals and structures. a**, **b**, Spatial distribution profiles of the VBM (**a**) and CBM (**b**) in the ground state in the MOF single cell at an isosurface value of $0.003 \text{ e} \text{ Å}^{-3}$. Yellow bubbles and green bubbles represent the electron clouds. **c**, **d**, The dihedral angles (involving the linker atoms of C1–C2–C3–C4) of the CBM linker in the CFA-Zn structure in the ground state (**c**) and excited state (**d**) are 46.3° and 28.4°. **e**, **f**, Spatial distribution profiles of the VBM (**e**) and CBM

(f) in the excited state in the MOF single cell at an isosurface value of 0.003 e Å⁻³. Purple bubbles and dark blue bubbles represent the electron clouds. Hydrogen atoms and acetate are omitted for clarity. Carbons in crystallographically different linkers are represented in orange and bright blue. Nitrogen and zinc are shown in blue and green, respectively.

The temperature-dependent conductivity curves and calculated density of states (DOS) reflect the semiconductor-like behaviour of the MOF (Supplementary Figs. 7 and 8)²⁸, supporting the existence of a photoinduced charge-transfer process. In photocatalysis, charge migration occurs between the valence and conduction bands, for example, a transition from the valence band maximum (VBM, corresponding to the highest occupied molecular orbital, HOMO) to the conduction band minimum (CBM, corresponding to the lowest unoccupied molecular orbital, LUMO) under the lowest energy excitation (Supplementary Discussion 2). The structure of CFA-Zn is highly asymmetric (space group P321), with two crystallographically distinct linkers that are chemically equivalent. Based on density functional theory (DFT) calculations, the CBM and VBM of ground-state CFA-Zn are located on crystallographically independent linkers and do not overlap (Fig. 2a,b), demonstrating the chemical segregation of band edges. Further wavefunction analysis combined with time-dependent ab initio non-adiabatic molecular dynamics (NAMD) simulations suggest charge transition still takes place between the chemically segregated energy bands even under higher energy excitations (Supplementary Figs. 9-12 and Supplementary Discussion 2). Unlike MOFs with open-shell metal nodes that share excited electrons with organic linkers, here the Zn²⁺ nodes with closed-shell d¹⁰ configuration refuse to accommodate extra electrons. Therefore, the CBM linker will entirely accept the energy of an excited electron, inducing the linker to undergo structural twisting, that is, the dihedral angle significantly changes from 46.3° and 28.4° (Fig. 2c,d). This prompts excited-state orbital rearrangement. In other words, for an optimal system energy, both CBM and VBM wavefunctions are located on the same linker (the original CBM linker in the ground state, as in Fig. 2e, f) in the excited state²⁹. As a result, substantial change occurs to the potential energy surface, and the relaxation channel from the excited state to the original ground state is broken^{17,30}. This thus shuts down the backward charge transfer from the excited acceptor to the ground-state donor through radiative relaxation. Therefore, long-lived charge separation is achieved in CFA-Zn (Supplementary Fig. 13 and Supplementary Discussion 3). Furthermore, the fluorescence lifetime of CFA-Zn varies with the viscosity of the solvent (Supplementary Figs. 14). This variation arises because the structural twisting rate of CFA-Zn competes with the rate of charge recombination, supporting the role of dynamic structural twisting in suppressing charge recombination. Based on the Tauc equation and Mott–Schottky results, the energy levels of the CBM and VBM were estimated to be -1.08 V and 2.19 V versus NHE, respectively (Supplementary Figs. 15 and 16), meeting the thermodynamic requirements for visible-light OWS.

Photocatalytic performance

To validate the thermodynamics of CFA-Zn related to water splitting, the photocatalytic half-reactions of H₂ and O₂ production were examined over in situ photodeposited Pt/CFA-Zn. The photocatalytic H₂ and O₂ production rates were ~527.7 and ~422.6 μ mol g⁻¹in 3 h, respectively, in the presence of appropriate sacrificial agents (Supplementary Fig. 17), confirming that the MOF fulfils the thermodynamic criteria for OWS. Encouraged by this, photocatalytic water splitting without sacrificial agents was attempted. Visible-light photocatalytic OWS activity over pristine CFA-Zn was low due to high overpotential; only ~18.0 µmol g⁻¹H₂ was produced in 12 h. Possible catalytic sites in the linkers were uncovered by DFT calculations (Supplementary Figs. 18-21). To reduce the overpotential, platinum nanoparticles were photodeposited in situ as a reduction co-catalyst and presynthesized Co₃O₄ was introduced as an oxidation co-catalyst, yielding Pt/CFA-Zn/Co₃O₄ (Supplementary Figs. 22-28 and Supplementary Discussion 4). To verify charge transfer between CFA-Zn and co-catalysts, in situ X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (sXAS) were performed. Upon light irradiation, a shift towards lower binding energy is observed in the Pt 4f peaks (Supplementary Fig. 29), indicating the electron transfer from the MOF to platinum³¹. In addition, an enhanced signal of cobalt after light irradiation can be detected by in situ sXAS, which implies transfer of holes from the MOF to Co₃O₄ (Supplementary Fig. 30)³².

Photocatalytic OWS began with an induction period due to the photodeposition of platinum and the slow diffusion of gas products



Fig. 3 | Photocatalytic performance. a, Photocatalytic OWS activity over Pt/CFA-Zn/Co₃O₄ under visible-light irradiation. Inset: enlargement of the induction period. **b**, AQE as a function of incident light wavelength in photocatalytic OWS over Pt/CFA-Zn/Co₃O₄. The error bars indicate the mean \pm s.d. calculated from three independent measurements. **c**, Mass spectrum

(Fig. 3a and Supplementary Fig. 31)⁶. Notably, during this initial stage (≤ 1.75 h), H₂ and O₂ were produced simultaneously in a stoichiometric molar ratio of ~2:1, confirming that OWS is occurring. Unfortunately, the amount of O₂ did not steadily increase as expected, possibly because O₂ was consumed in side reactions, which commonly occurs when noble metals are used as co-catalysts^{6,10–12}. After 12 h, 5.98 µmol H₂O₂ was detected in the reaction solution, verifying that side reactions were consuming O₂ (Supplementary Fig. 32 and Supplementary Discussion 5). The hydrogen production rate of CFA-Zn reached 102.8 µmol g⁻¹ h⁻¹ under visible-light irradiation, with AQEs of 3.09 ± 0.32% (365 nm) and 2.12 ± 0.26% (380 nm) (Fig. 3b and Supplementary Discussion 6).

of O₂ gas evolved by photocatalytic OWS using 97% ¹⁸O-labelled water. **d**, Long-time (100 h) recycling performance of CFA-Zn during ten consecutive runs with evacuation every 10 h. **e**, A comparison of the AQE and the stability of Pt/CFA-Zn/Co₃O₄ (this work) with those of other reported OWS photocatalysts. See Supplementary Table 2 for details.

Control experiments further prove that the reaction products originate from water splitting rather than catalyst degradation (Supplementary Table 1). The results of the N₂ reference (Fig. 3a, black line) and ¹⁸O-labelled experiments unambiguously demonstrate that the O₂ is produced from water splitting rather than air leakage (Fig. 3c and Supplementary Fig. 33). Although typical visible-light-responsive inorganic semiconductors, such as (oxy)nitrides and (oxy)sulfides, suffer from severe deactivation during photocatalysis, CFA-Zn does not display significant activity loss during ten consecutive runs that lasted 100 h (Fig. 3d and Supplementary Figs. 34 and 35), demonstrating good photostability. The photocatalytic activity of CFA-Zn with co-catalysts is among the highest reported for one-step excitation

MOF photocatalysts, and the activity and stability of CFA-Zn compare very favourably with other photocatalysts for visible-light-responsive OWS (Fig. 3e and Supplementary Table 2).

Under the same conditions, representative MOFs that have been extensively investigated as photocatalysts do not display observable activity (Supplementary Table 3). It is noteworthy that although MOFs have been intensively studied, and are recognized to be promising photocatalysts for water splitting, sacrificial reagents are generally required²²⁻²⁵. Indeed, very few examples of photocatalytic OWS over a single MOF, where the mechanism is basically related to a linker-to-metal charge-transfer (LMCT) process, have been reported³³⁻³⁵. In previously reported MOF photocatalysts, although empty d-orbitals of open-shell metal nodes may serve as channels for electron transfer, they can also become centres for charge recombination³⁶. Therefore, separating electrons and holes that are distributed in interconnected open-shell metal nodes and linkers has proven challenging. In contrast, by adopting closed-shell Zn²⁺, the adoption of a linker-to-linker charge transfer (LLCT) process in CFA-Zn gives rise to a long-lived, charge-separated state and enhanced activity.

Significance of dynamic structural twist

To shed light on the significance of the dynamic structural twisting of CFA-Zn in photocatalysis, the linkers in CFA-Zn are gradually substituted with 4,4'-dimethyl-1H,1'H-5,5'-bibenzo[d][1,2,3]triazole (bibta-2CH₃), resulting in CFA-Zn-nCH₃ (n = 1-6) (Supplementary Figs. 36 and 37). The loading amount of bibta-2CH₃ in the resulting MOF is determined by ¹H NMR (Supplementary Fig. 38 and Supplementary Table 4). The introduction of the -CH₃ groups imparts additional steric hindrance compared with the parent CFA-Zn, thereby constraining the flexibility of linkers within the MOF. The strongly suppressed linker twisting has been confirmed by theoretical calculations (Supplementary Fig. 39). Furthermore, time-resolved photoluminescence spectra suggest that the lifetime of photogenerated carriers decreases along with increased content of bibta-2CH₃ linkers in the resulting MOF (Supplementary Fig. 40), experimentally demonstrating the importance of the structural twist for charge separation. As expected, CFA-Zn-nCH₃ showcase gradually reduced OWS activity compared with CFA-Zn, along with increased concentrations of bibta-2CH3 linkers, and eventually disappear (Supplementary Fig. 41). The results unambiguously support the importance of dynamic structural twisting in photocatalytic OWS.

Roles of structural asymmetry

The arrangement of band edges (that is, VBM and CBM) in a photocatalyst profoundly affects the efficacies of charge separation and recombination. The aforementioned DFT calculations locate the VBM and CBM of CFA-Zn on chemically equivalent yet crystallographically independent linkers; the zinc nodes are not involved in the band edges at all (Fig. 2a,b). Therefore, the band edges are segregated, which is a prerequisite for an excited-state structural twist. To elucidate the role of structural asymmetry in suppressing charge recombination, the energy band configurations of ZIF-8 and MFU-41 that involve d¹⁰ metal nodes and azole-based linkers, similar to CFA-Zn, yet possess symmetric structures, have been investigated (Supplementary Figs. 42-46). In sharp contrast to CFA-Zn, the band edges of ZIF-8 and MFU-4l are significantly overlapped, and accordingly photocatalytic OWS activity cannot be detected (Supplementary Table 3), demonstrating the importance of the asymmetric structure of CFA-Zn for the complete separation of band edges.

Photocatalysis involves electron transfer from light-harvesting units to catalytic units. The exposed facets with distinct electronic structures strongly influence charge transfer and OWS activity³⁷. Given the particular morphology of CFA-Zn, the crystallographically independent linkers might distribute onto different facets, leading to varying degrees of VBM and CBM character on different facets. The projections of the VBM and CBM on different facets by DFT calculations clearly reveal that excited electrons (in the CBM) primarily migrate to the (001) facet (Fig. 4a,b and Supplementary Figs. 47–49). This is supported by the largest work function and the lowest CBM position of the (001) facet among all the facets (Supplementary Fig. 50 and Supplementary Table 5)³⁷, which is experimentally evidenced by the fact that the platinum nanoparticles were reduced in situ on the (001) facet by photogenerated electrons (Supplementary Fig. 51). The high work function of platinum leads to Schottky contact with the MOF, intensifying the charge imbalance between the (001) and other facets, thereby accelerating electron transfer to the (001) facet. Consequently, Pt/CFA-Zn with selectively photodeposited platinum on the (001) facet demonstrates a charge separation efficiency and activity superior to those of Pt_{imp}/CFA-Zn (Supplementary Figs. 52-55), in which platinum nanoparticles are supported on arbitrary facets by the impregnation method (Supplementary Fig. 56 and Supplementary Discussion 7). Photon-irradiated Kelvin probe force microscopy was used to investigate the distribution of photogenerated electrons³⁸. Compared with the unchanged surface photovoltage (SPV) potential of the parent MOF under light irradiation (Supplementary Figs. 57 and 58), a significant negative potential of approximately -100 mV was measured on the (001) facet of Pt/CFA-Zn (Fig. 4c,d and Supplementary Fig. 59); this negative potential validates the distribution of more electrons throughout the (001) facet.

Mechanism of long-lived charge separation

Proton migration occurs nearly concurrently with electron transfer in photocatalysis. It is expected that in CFA-Zn, protons will migrate from the VBM, where H₂O oxidation occurs, to the CBM to participate in H₂ generation, in a manner analogous to proton migration from photosystem II to photosystem I during natural photosynthesis. To verify the proton migration dynamics (Supplementary Fig. 60a), a metadynamics simulation was conducted³⁹. The results confirm that protons migrate along the expected path from the VBM to the CBM in ~2.5 ps (Supplementary Fig. 60b), featuring a barrier of 0.719 eV that is readily overcome (Fig. 4e)⁴⁰.

To illustrate the importance of closed-shell metal nodes for forbidding radiative relaxation, Zn²⁺ in CFA-Zn was partially replaced with Co^{2+} by postsynthetic exchange (CFA-Zn/Co_n, n = 0.08, 0.20, 0.64, n = Co/Zn molar ratio (Supplementary Fig. 61). Open-shell Co²⁺ can act as an electron channel to connect the chemically segregated linkers. Accordingly, all cobalt-substituted MOFs exhibited activities inferior to CFA-Zn, with activity dramatically decreasing with increasing cobalt substitution (Fig. 5a). Although the in situ electron paramagnetic resonance (EPR) spectrum of CFA-Zn shows a free electron signal only (Supplementary Fig. 62), reduced Co(II) EPR signals can be observed in the cobalt-substituted MOF (Supplementary Fig. 63), indicating that cobalt nodes are able to accept electrons. Moreover, in situ sXAS of CFA-Zn/Co_{0.64} was adopted to probe the photogenerated charge transfer. Under light irradiation, the intensities of L₃ and L₂ for cobalt are clearly reduced (Fig. 5b), supporting that the cobalt nodes accept electrons³². In contrast, the sXAS signals for the zinc nodes remain consistent, confirming that zinc is not involved in the charge transfer (Supplementary Fig. 64). The in situ sXAS results reinforce the LLCT process in CFA-Zn, and the substitution of zinc with cobalt species in the zinc nodes can introduce LMCT and disrupt the LLCT process. Partial DOS results reveal the involvement of cobalt in the formation of band edges (Supplementary Figs. 65 and 66), and the overlap between the VBM and the CBM apparently increases (Supplementary Figs. 67-70). On this occasion, the energy of an excited electron is distributed throughout not only the VBM and CBM linkers but also the cobalt nodes. Consequently, the altered energy is insufficient to trigger the structural rearrangement forbidding radiative relaxation³⁰, as evidenced by the fact that the observed structural twist in excited CFA-Zn nearly disappears after introducing cobalt (Supplementary Table 6). DFT calculations show that the excited electrons in CFA-Zn/Co_n are readily consumed via radiative relaxation (Fig. 5c and Supplementary



H-N1 distance (Å)

Fig. 4 | **Charge separation and proton migration performance. a,b**, Projections of the VBM (**a**) and the CBM (**b**) onto the (001) facet of CFA-Zn. The colour bar represents the charge density (a.u.). Carbon, nitrogen and zinc atoms are coloured in orange, blue and green, respectively. Hydrogen atoms and acetate are omitted for clarity. The same colour scheme is used in **e**.

 ${\bf c}, {\tt Photon-irradiated\,Kelvin\,probe\,force\,microscopy\,image\,of\,{\tt Pt/CFA-Zn\,obtained}$

by subtracting the surface potential in the dark from the surface potential under light irradiation. The colour bar represents the SPV signals. **d**, The corresponding SPV profiles measured along the black dashed line in **c** under various conditions. **e**, Free energy as a function of the H–NI distance (VBM) and the H–N2 distance (CBM). The values –1.092, –0.373 and –0.911 represent the energies of the proton in its initial, transition and final states, respectively.

Fig. 71), which provides further evidence that the cobalt site acts as a channel for charge recombination, thereby breaking the chemically segregated state between the VBM and CBM units. By breaking the well-accepted LMCT mechanism in MOF photocatalysis, the previous results unambiguously demonstrate that the LLCT process would be ideal for creating a chemically segregated state capable of suppressing charge recombination and offering enhanced photocatalysis.

The electron-hole recombination time in CFA-Zn and CFA-Zn/ Co₄ was evaluated using time-dependent ab initio NAMD simulations (Fig. 5d). As expected, in CFA-Zn/Co₄, 80% of excited electrons were rapidly depleted in less than 30 fs, indicating that photoexcited electrons are too unstable to be utilized in photocatalysis. In sharp contrast, fewer than 3% of excited electrons in CFA-Zn were depleted after 2,000 fs, which is on the same time scale as that for proton transfer (Supplementary Fig. 60b). These results indicate that the use of closed-shell Zn²⁺ nodes extends the excited-state lifetime far more than 1,000-fold, in effect forbidding the backward transition from the excited acceptor to the donor. To experimentally validate the NAMD simulation results, femtosecond transient absorption spectra and time-resolved photoluminescence spectra of CFA-Zn and CFA-Zn/Co_{0.2} were collected. The ultraviolet-visible absorption was similar whether or not cobalt was introduced (Supplementary Fig. 72), suggesting that the presence of cobalt does not greatly affect light absorption. More importantly, the comparison of the excited state kinetics at 650 nm (that is, the peak position of the excited-state absorption profiles in Supplementary Fig. 73) indicates that the average relaxation lifetime of CFA-Zn $(102 \pm 4 \text{ ps})$ is much longer than that of CFA-Zn/Co_{0.2} (59 ± 1 ps), reflecting the significant suppression of charge recombination in CFA-Zn (Fig. 5e and Supplementary Table 7)⁴¹, which is in line with the NAMD simulation results. Furthermore, the longer fluorescence lifetime observed in CFA-Zn also supports the suppressed charge recombination in comparison with CFA-Zn/Co_{0.2} (Supplementary Fig. 74).



Fig. 5 | **Performance comparison of CFA-Zn and CFA-Zn/Co_n. a**, The photocatalytic H_2 production rates of CFA-Zn/Co_n as a function of Co/Zn molar percentage in the photocatalytic OWS. The number labels represent the Co/Zn molar percentage. **b**, In situ Co L-edge sXAS spectra for CFA-Zn/Co_{0.64} in the dark and under light irradiation. **c**, A schematic diagram contrasting the long-lived

Strategy generalizability

To assess the generalizability of such a chemically segregated state for forbidding radiative relaxation in OWS photocatalysts, two other MOFs, namely, Cd(5-BrIP)(TIB) (Supplementary Fig. 75)⁴² and JNU-402-NH₂ (Supplementary Fig. 76)⁴³, have been examined. The skeletons of these MOFs are comprised of closed-shell d^{10} metal ions connected by two different linkers. DFT calculations reveal that their band edges are chemically segregated (Supplementary Figs. 77 and 78), which induces a structural twist upon photoexcitation (Supplementary Figs. 79 and 80), guaranteeing that radiative relaxation is forbidden (Supplementary arising from charge recombination induced through radiative relaxation.

CFA-Zn/Co₄. e, Femtosecond transient absorption (TA) kinetics of CFA-Zn and

 $CFA-Zn/Co_{0.2}$ at 650 nm, and the corresponding average relaxation lifetimes.

d, Non-radiative electron-hole recombination dynamics in CFA-Zn and

Conclusion

This work reports that dynamic structural twisting of photocatalysts in an excited state can induce forbidden radiative relaxation and lead to a long-lived, charge-separated state. Although higher OWS efficiencies have been reported^{9–12}, we believe that future investigations following this approach of creating dynamic microenvironment, along with minimizing non-radiative relaxation, improving charge transfer and

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optimizing the reaction parameters, will further enhance photocatalytic OWS activity.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41557-024-01599-6.

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Methods

Synthesis of CFA-Zn

The MOF was synthesized following a previously reported method with some modifications⁴⁴. Typically, 1.48 g zinc acetate dihydrate and 0.40 g H₂bibta were dissolved in a mixed solvent of 0.20 l*N*,*N*-dimethylformamide (DMF) and 8.00 ml acetic acid, and then heated to 120 °C for 48 h. After cooling the mixture to room temperature, the sample was washed sequentially with DMF, methanol and acetone. Finally, the product was activated under vacuum for 12 h at 150 °C.

Synthesis of CFA-Zn-nCH₃

CFA-Zn-nCH₃ (n = 1-6) was prepared by a postsynthetic exchange method. For n = 1-3.50.0 mg CFA-Zn was dispersed into 10.0 ml DMF in a 20 ml glass vial. Subsequent introduction of H₂ bibta-2CH₃ were performed in quantities of 3.1 mg (0.013 mmol), 6.2 mg (0.023 mmol) and 30.5 mg (0.115 mmol). After ultrasonication, the mixtures were heated to 120 °C for 48 h. After cooling the mixtures to room temperature, the products were washed sequentially with DMF and acetone five times. Finally, the product was activated under vacuum for 12 h at 150 °C. To further increase the content of bibta-2CH₃ in the resulting MOFs, the linker exchange process was repeated under different conditions. For n = 4, 50 mg CFA-Zn-3CH₃ was dispersed into 5.0 ml methanol in a round-bottom flask, and then 30.5 mg H₂bibta-2CH₃ was added. The mixtures were refluxed with stirring at 70 °C for 48 h. For n = 5,50 mg CFA-Zn-4CH₃ was dispersed into 5.0 ml acetonitrile in a round-bottom flask, and then 30.5 mg H₂bibta-2CH₃ was added. The mixtures were refluxed with stirring at 85 °C for 24 h. For n = 6,50 mg CFA-Zn-5CH₃ was dispersed into a mixture of 4.0 mL acetonitrile and 1 ml H₂O in a 30 ml microwave vessel, and then 30.5 mg H_2 bibta-2CH₃ was added. The reaction was heated to 80 °C by microwave reactor, and held at this temperature for 24 h under continuous stirring.

Quantification of H₂bibta-2CH₃ in CFA-Zn-*n*CH₃

The content of H_2 bibta-2CH₃ in CFA-Zn-*n*CH₃ was determined by ¹H NMR. Typically, 4.0 mg CFA-Zn-nCH₃ was dispersed into 0.50 ml d⁶-DMSO. Subsequently, 20.0 μ l of H_2 SO₄ was introduced to the solution. Upon heating, a settled and transparent solution was obtained for subsequent ¹H NMR analysis.

Preparation of Pt/CFA-Zn

Typically, 50.0 mg CFA-Zn was placed in a quartz reactor containing 70.00 ml water and 10.00 ml methanol, and then 0.20 ml H₂PtCl₆·6H₂O aqueous solution (20 mg ml⁻¹) was added. After purging with N₂ for 20 min to remove air, the reaction vessel with reacting solution was fixed and irradiated with a 300 W xenon lamp for 30 min. The as-prepared sample was washed with methanol and dried at 85 °C to afford Pt/CFA-Zn. The platinum content was 2.87 wt% as quantified by inductively coupled plasma mass spectrometry (ICP-MS).

Preparation of Pt_{imp}/CFA-Zn

Typically, 50.0 mg CFA-Zn was dispersed into 10.00 ml methanol, and then 0.21 ml H₂PtCl₆·6H₂O aqueous solution (20 mg ml⁻¹) was added. The solution was stirred for 2 h and then collected by centrifugation. The obtained sample was reduced by H₂ at 180 °C for 2 h to afford Pt_{imp}/ CFA-Zn. The platinum content was 2.91 wt% as quantified by ICP-MS.

Preparation of CFA-Zn/FTO

Fluorine-doped tin oxide (FTO) glass was ultrasonically washed with ethanol. Specifically, 19.0 mg zinc acetate dihydrate and 5.0 mg H₂bibta were dissolved in a mixed solution of 10.00 ml DMF and 50.0 μ l acetic acid. The mixed solution was ultrasonically dissolved, and then the FTO glass was put into the solution. The reaction system was heated at 120 °C for 2 days. Finally, the FTO glass (with CFA-Zn grown on it) was washed with methanol and dried at 85 °C.

Preparation of Pt/CFA-Zn/FTO

The CFA-Zn/FTO was placed in a quartz reactor containing 18.00 ml acetonitrile and 2.00 ml methanol. Then, 7.0 μ l H₂PtCl₆·6H₂O aqueous solution (20 mg ml⁻¹) was added. After purging with N₂ for 20 min to remove air, the reaction vessel with the reaction solution was fixed, and irradiated by a 300 W xenon lamp for 30 min. The as-prepared sample was washed with methanol and dried at 85 °C.

Preparation of CFA-Zn/Co

Typically, 50.0 mg CFA-Zn was dispersed in 10.00 ml DMF in a glass vial. Following that, 2.5, 50.0 or 100.0 mg $Co(CH_3COO)_2$ ·4H₂O was added. The reaction vial was then sealed and reacted at 60 °C for 24 h under stirring to yield CFA-Zn/Co_n (n = 0.08, 0.2, 0.64; n represents the molar ratio of Co/Zn; the amounts of zinc and cobalt were determined by ICP-MS). The product was collected by centrifugation, washed with DMF until the solution was colourless and then washed with acetone three times. Finally, the product was activated under vacuum for 12 h at 150 °C.

Photocatalytic experiments

All photocatalytic experiments were conducted on an online system (LabSolar-6AG, PerfectLight, Beijing Perfectlight Technology) with a 300 W xenon lamp (LX-300F) as the light source.

Photocatalytic hydrogen production (half reaction). The photocatalytic hydrogen production experiments were carried out in a 250 ml quartz reactor with stirring at 10 °C using a 300 W xenon lamp (LX-300F) equipped with an ultraviolet cut-off filter (>380 nm). Typically, 30.0 mg CFA-Zn was dispersed in 70.00 ml deionized water with 10.00 ml methanol as a sacrificial reagent, and then 0.12 ml $H_2PtCl_6\cdot 6H_2O$ aqueous solution (20 mg ml⁻¹; platinum theoretical loading, 3.0 wt%) was added. Prior to the photocatalytic activity test, the suspension was thoroughly degassed to remove air. Hydrogen gas was measured by gas chromatography (Shimadzu GC-2014; argon as a carrier gas) using a thermal conductivity detector (TCD). The produced hydrogen was quantified by a calibration plot.

Photocatalytic oxygen production (half reaction). The photocatalytic oxygen production experiments were carried out in a 250 ml quartz reactor with stirring at 10 °C using a 300 W xenon lamp (LX-300F) equipped with an ultraviolet cut-off filter (>380 nm). Typic cally, 30.0 mg Pt/CFA-Zn and 0.10 g AgNO₃ were dispersed in 80.00 ml deionized water. Prior to the photocatalytic activity test, the suspension was thoroughly degassed to remove air. Oxygen gas was measured by gas chromatography (Shimadzu GC-2014; argon as a carrier gas) using a TCD. The produced oxygen was quantified by a calibration plot.

Photocatalytic water overall splitting. The photocatalytic OWS experiments were carried out in a 250 ml quartz reactor with stirring at 20 °C using a 300 W xenon lamp (LX-300F) equipped with an ultraviolet cut-off filter (>380 nm). Typically, 30.0 mg CFA-Zn (or 30.0 mg Cd(5-BrIP)(TIB) or 30.0 mg JNU-402-NH₂) was dispersed in a mixed solution of 72.00 ml deionized water and 8.00 ml DMF (for promoting MOF dispersion in water). Then, $0.12 \text{ ml H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution $(20 \text{ mg ml}^{-1}; \text{platinum theoretical loading}, 3.0 \text{ wt\%})$ and 0.31 ml Co₃O₄ dispersed solution (2 mg ml⁻¹; Co₃O₄ theoretical loading, 2.0 wt%) were added. Prior to the photocatalytic activity test, the suspension was thoroughly degassed to remove air. Hydrogen and oxygen gases were measured by gas chromatography (Shimadzu GC-2014; argon as a carrier gas) using a TCD. The produced gas was quantified by a calibration plot. The AQY of the overall water splitting was measured using a xenon lamp with monochromatic light filters. The light intensity was measured by a radiometer (Beijing Normal University, FZ-A) and the result is the average of five test points. The AQY was calculated by using the equation: $AQY(\%) = [2 \times n(H_2)]/n(photons) \times 100$, where

 $n(H_2)$ and n(photons) represent the number of H_2 and the number of incident photons, respectively. Prior to testing the AQY and the recycling performance, the system was irradiated for 2 h to deposit the platinum co-catalyst.

The ¹⁸**O**₂ **isotope experiment.** Photocatalytic H₂¹⁸O splitting to trace ¹⁸O₂ was carried out in a sealed 20 ml quartz tube. Typically, 5.0 mg CFA-Zn was dispersed in 5.00 ml H₂¹⁸O, and then 20.0 μ l H₂PtCl₆·6H₂O solution (20 mg ml⁻¹; Pt theoretical loading, 3.0 wt%) and 52.0 μ l Co₃O₄ dispersed solution (2 mg ml⁻¹; Co₃O₄ theoretical loading, 2.0 wt%) were added. Prior to the photocatalytic activity test, the suspension was degassed with argon to remove air. The gas products in the headspace of the quartz tube were analysed by gas chromatography–mass spectrometry (7890A-5975C, Agilent).

 H_2O_2 detection method. The amount of H_2O_2 formed in the reaction mixture was quantified by a colorimetric method⁴⁵. First, an H_2O_2 standard solution or the reaction solution was added to a mixed solution containing 1.00 ml of 0.50 M H_2SO_4 and 0.10 ml of 15 wt% TiO(SO₄) solution (0.50 M H_2SO_4). Then, the mixed solution was diluted to 10.00 ml. The absorbance of H_2O_2 solutions was recorded with a Shimadzu UV-2700.

Computational details

DFT calculation. The structural models of CFA-Zn and CFA-Zn/Co, were obtained from the reported structure²⁷. Subsequently, the ground state and excited structures were optimized using the CP2K 9.1.0 program⁴⁶. The Quickstep method⁴⁷ was utilized to compute the energy of a system by using Kohn-Sham (KS) DFT⁴⁸ with the non-empirical Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The Grimme-D3 dispersion correction was applied to illustrate van der Waals interactions. To describe the interactions between the core electrons, the Goedecker-Teter-Hutter pseudopotentials⁴⁹ were used in the calculations. The localized double ξ -valence-polarized basis set⁵⁰ was chosen to expand the wavefunctions with a plane-wave cut-off of 500 Ry. To obtain the work functions for different facets of CFA-Zn, Material Studio software was used to construct the (001), (110), (210) and (211) facets. The damaged rings were repaired, and the hydrogen atoms at the end of the unsaturated groups were added. The vacuum space was set to be approximately 20 Å to ensure sufficient separation between periodic images of the system. Then, the electronic configurations of these facets were optimized by CP2K software. The hybrid functional of Heyd. Scuseria and Ernzerhof (HSE06) was used to calculate the work function and the CBM positions of different facets. To address the polarization effects on the surface, a surface dipole correction was applied.

To obtain more accurate results, the hybrid functional of HSE06 was used to calculate the partial DOS^{51} , and the band edges (VBM/ CBM) for CFA-Zn and CFA-Zn/Co_n by the Vienna Ab initio Simulation Package (VASP) with an energy cut-off of 400 eV. Grimme's DFT-D3 method was adopted for the long-range van der Waals interaction corrections. The projector-augmented wave method⁵² was implemented for plane-wave expansion. The electron energies along the reaction pathways in the hydrogen production and oxygen production processes were calculated using the PBE functional⁵³. The Brillouin zone was sampled with a $1 \times 1 \times 1$ Monkhorst–Pack *k*-mesh. The forces and energies of the geometric structures were converged to 0.01 eV Å⁻¹ and 10^{-5} eV, respectively.

Calculation for the free energies. Based on the general single site of the oxygen evolution reaction mechanism, the four electron–proton transfer steps involved in the whole reaction can be written as (* represents catalytic sites):

$$* + H_2O(l) \rightarrow OH^* + H^+ + e^-$$
 (1)

$$OH^* \rightarrow O^* + H^+ + e^-$$

(2)

$$O^* + H_2O(1) \rightarrow OOH^* + H^+ + e^-$$
 (3)

$$OOH^* \to * + O_2 + H^+ + e^-$$
 (4)

The dual-site route, which was more favourable for the CFA-Zn catalysts (Supplementary Fig. 20), contains five elementary steps and can be depicted as:

$$H_{2}^{*} + H_{2}O(1) \rightarrow OH^{*} + H^{+} + e^{-}$$
 (5)

$$OH^* \to O^* + H^+ + e^-$$
 (6)

$$O^* + H_2O(I) \rightarrow O^*OH^* + H^+ + e^-$$
 (7)

$$O^*OH^* \to O^*O^* + H^+ + e^-$$
 (8)

$$0^* 0^* \to * + 0_2 + e^-$$
 (9)

Meanwhile, the hydrogen evolution reaction mechanism contains two one-electron steps:

$$* + H^+ + e^- \to H^*$$
 (10)

$$H^* + H^+ + e^- \rightarrow * + H_2$$
 (11)

To calculate the free energy changes, the standard change of Gibbs free energy at zero potential was calculated according to the following equation 54 :

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{12}$$

where ΔE is the change of reaction energy based on DFT simulations, Δ ZPE is the zero-point energy change calculated by the vibrational frequency using the finite-difference method and ΔS represents the entropy change for each elementary step. The temperature in our work is set to 298.15 K.

Ab initio NAMD simulations. The charge evolution of the structures was performed by Hefei-NAMD with a surface-hopping algorithm⁵⁵. The structural trajectories of CFA-Zn and CFA-Zn/Co were simulated over 6.0 ps by VASP with ab initio molecular dynamics. The equilibrium temperature was set to 300 K with a time step of 1 fs. One hundred different initial configurations were selected to simulate the NAMD results, and each chosen configuration was sampled for 2×10^4 trajectories at the last 3.0 ps. The wavefunctions for 3,000 configurations were obtained using the PBE functional.

The dynamics of photogenerated carriers are determined by NAMD implemented in time-dependent DFT within the KS frame-work⁵⁶⁻⁵⁸. For our system, one electron will initially be excited to the conduction band edge of CFA-Zn or CFA-Zn/Co, and then relax to the CBM. The charge of the hybrid system can be obtained from the time-dependent single-particle KS orbital:

$$\rho(\mathbf{r},t) = \sum_{p=1}^{N_{\rm c}} \left| \psi_p(\mathbf{r},t) \right|^2 \tag{13}$$

where $p = 1, 2, ..., N_e$, N_e is the number of electrons, **r** represents electron motion and $\psi_p(\mathbf{r}, t)$ is the wave function of the excited electron. Based on the time-dependent variational principle, a set of single-electron equations for the evolution of the KS orbital can be obtained, which determines the evolution of the electron density:

$$i\hbar \frac{\partial \psi_p(\mathbf{r}, t)}{\partial t} = H(\mathbf{r}, \mathbf{R}, t) \psi_p(\mathbf{r}, t)$$
(14)

where **R** represents nuclear motion. The time-dependent KS orbitals, $\psi_p(\mathbf{r}, t)$, can be expanded by a set for the adiabatic KS basis, $\phi_k(r, R(t))$, which is the wave function and eigenvalues for electron states *k*:

$$\Psi_{p}(\mathbf{r},t) = \sum_{k} c_{k}(t) \phi_{k}(\mathbf{r},\mathbf{R}(t))$$
(15)

The evolution of the expanding coefficients for the adiabatic basis can be calculated by inserting equation (15) into equation (14):

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t) \left(\varepsilon_k \delta_{jk} + d_{jk} \right)$$
(16)

where ε_k is the energy of the adiabatic state and d_{jk} is the non-adiabatic coupling between states *j* and *k*:

$$d_{jk} = \left\langle \phi_j \left| \frac{\partial}{\partial t} \right| \phi_k \right\rangle = \frac{\left\langle \phi_j \left| \nabla_R H \right| \phi_k \right\rangle}{\varepsilon_k - \varepsilon_j} \dot{R}$$
(17)

where *H* is the KS Hamiltonian, *R* is the position of the nuclei and \dot{R} is the velocity of the nuclei.

The contribution of non-adiabatic and adiabatic coupling to charge transfer can be obtained by inserting equation (15) into equation (13) and taking the time derivative of equation (13):

$$\frac{\mathrm{d}f_{\mathrm{Janus}}\rho_{\mathrm{p}}(\mathbf{r},t)\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \sum_{ij} \left\{ \frac{\mathrm{d}(c_{i}^{*}c_{j})}{\mathrm{d}t} \int_{\mathrm{Janus}} \phi_{i}^{*}\phi_{j}\mathrm{d}\mathbf{r} + c_{i}^{*}c_{j}\frac{f_{\mathrm{Janus}}\phi_{i}^{*}\phi_{j}\mathrm{d}\mathbf{r}}{\mathrm{d}t} \right\}$$
(18)

The first term represents the population change of each adiabatic state, which is defined as the contribution of non-adiabatic coupling to charge transfer; the second term represents the change of charge density caused by localization of the KS adiabatic state, which can be attributed to the contribution of adiabatic coupling.

Well-tempered metadynamics simulation. To investigate the dynamic behaviour of the proton transition from the oxidation active site (VBM) to the reduction active site (CBM), a metadynamics simulation was carried out using the CP2K 9.1.0 program⁴⁶. The Nosé–Hoover method⁵⁹ with velocity rescaling was used to maintain the temperature in the NVT ensemble.

In this work, we adopted well-tempered metadynamics⁶⁰, and the reaction time scale was accelerated by adding a systematic biasing potential along a set of a few predefined collective variables (CVs) suitable for describing the reaction mechanism, where the distances N1–H and N2–H were chosen as CV1 and CV2, respectively (Supplementary Fig. 60). As the CVs were determined, the bias potential deposition was as follows:

$$V(S,t) = \left(k_{\rm B}\Delta T \ln\left(1 + \frac{\omega N(S,t)}{k_{\rm B}\Delta T}\right)$$
(19)

where V(S,t) and N(S,t) represent the time derivative of the bias potential and the histogram of the *S* variables collected during the simulation, respectively, and $k_{\rm B}$ is the Boltzmann constant. Here, ΔT is an input parameter with the dimension of a temperature and was set to 2,400 K; thus the bias deposition rate will decrease over the simulation time. ω denotes the energy rate, which is constant and is usually expressed in terms of a Gaussian height (*W*) and a deposition stride ($\tau_{\rm G}$). In well-tempered metadynamics, the height of the Gaussian is decreased with the amount of bias already deposited according to:

$$W = \omega \tau_{\rm G} e^{-\frac{V_{\rm G}(5,t)}{k_{\rm B} \Delta T}}$$
(20)

The Gaussian height was set to 0.003 Hartree, and the width was 10% that of the associated collective variable. The repulsive Gaussian

potential was placed every 30 fs. The metadynamics simulation was run at 300 K for 15 ps with a time step of 0.5 ps.

Data availability

Additional discussions and data supporting this article are available in the Supplementary Information. Source data are provided with this paper.

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Author contributions

H.-L.J. conceived the idea, and supervised and directed the project. K.S. and J.W. performed the experiments. Y.H. and J.J. performed the theoretical calculations. F.S. and F.F. conducted the photon-irradiated Kelvin probe force microscopy experiments. Q.W. and X.Z. helped with the synchrotron XPS and sXAS measurements. Q.Z. and Y.Z. studied the femtosecond transient absorption spectra. Y.L. provided constructive discussions. H.-L.J. and K.S. analysed the data and co-wrote the paper. All authors discussed the results and commented on the paper.

Competing interests

The authors declare no competing interests.

Additional information

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