

# A dynamic metal–organic framework photocatalyst

Photocatalytic overall water splitting (OWS) is highly desirable for hydrogen production but challenging owing to rapid charge recombination. We demonstrate a dynamic metal–organic framework (MOF) photocatalyst that achieves OWS via one-step photoexcitation. Upon excitation by light, the MOF undergoes a structural twist that suppresses charge recombination and achieves OWS.

## This is a summary of:

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## The problem

Achieving overall water splitting (OWS) using solar energy is a low-cost and easily scalable method for hydrogen production. However, the recombination rate of photogenerated electrons and holes in photocatalysts is considerably faster than the reaction rate of water splitting. This makes it challenging for water splitting to occur before the recombination of charge carriers, representing a critical bottleneck in the photocatalytic OWS process<sup>1</sup>. Many effective strategies have been developed to inhibit the recombination of electrons and holes during the photocatalytic process, such as doping, constructing heterojunctions, and crystal facet engineering<sup>1</sup>. However, most strategies target the ground-state structures and the recombination of electrons and holes in photocatalysis still occurs in the excited state. Suppressing charge recombination through regulating the excited state of the photocatalyst remains a considerable challenge.

## The discovery

In photosynthesis, photosensitive components absorb photons to generate excited-state electrons, which are subsequently transferred to terminal electron acceptors through a series of cofactors. During this process, the cofactors are often isolated, and upon receiving electrons undergo excited state structural changes to lower the system's energy, thereby extending the lifetime of the excited-state electrons<sup>2</sup>. This suggests that the specific reaction microenvironment is crucial for catalysis. Inspired by this mechanism, we designed a metal–organic framework (MOF) – which are known for their flexible structures and high tailorability<sup>3</sup> – to mimic the dynamic microenvironment in living organisms during photosynthesis and achieve a long-lived charge separation for photocatalytic OWS.

Our MOF, namely CFA-Zn, features two crystallographically independent linkers connected by Zn nodes (Fig. 1a). Under light irradiation, electrons are excited from one linker to the other, crystallographically distinct linker. Because Zn<sup>2+</sup> has a closed-shell configuration, there is no orbital overlap between the linkers on which the conduction band minimum (CBM) and valence band maximum (VBM) are located (Fig. 1b,c). Therefore, the CBM linker will entirely accept the energy of excited electrons, resulting in a high energy state in this linker. The flexibility of the MOF linker allows for dynamic structural twisting, which gives rise to reduced system energy and accordingly induces a rearrangement of the MOF's orbitals. This alters the potential energy surface, breaking

the relaxation pathway from the excited state to the original ground state. Accordingly, electron–hole recombination is prevented in CFA-Zn (Fig. 1d, left), achieving photocatalytic OWS with an apparent quantum efficiency of  $3.09 \pm 0.32\%$  at 365 nm. To support the importance of the closed-shell configuration of Zn in preventing the orbital overlap, which is crucial for inducing structural twist, partial substitution of Zn with open-shell Co leads to orbital overlap between the two crystallographically independent linkers. This overlap minimizes energy fluctuations caused by the excited-state electrons and alleviates linker twisting (Fig. 1d, right). Furthermore, deliberately introducing sterically hindered functional groups onto the linkers in the MOF skeleton inhibits linker twisting in the excited state and leads to reduced charge separation.

## Future directions

Photo-induced structural changes, such as chemical bond stretching and vacancy formation, are often crucial events in photocatalysis. Unfortunately, these changes are uncontrollable or challenging to observe for most photocatalysts. MOFs with flexible skeletons are promising structures for triggering dynamic structural change in photocatalysis. Moreover, MOFs have atomically precise structures, offering an excellent platform for capturing the dynamic behaviour of photocatalyst structures using advanced characterization techniques, such as serial femtosecond crystallography<sup>4</sup>.

Although photocatalytic OWS is achieved with this MOF, its photocatalytic performance still falls short compared to the most advanced photocatalysts. This may be attributed to severe non-radiative relaxation processes during the photocatalytic process. Additionally, the reliance on high-cost noble metals as co-catalysts to reduce the reaction overpotential remains a concern. There are several routes to further optimize MOFs for photocatalysis given the wide array of MOF structures available and the potential for further optimization of MOF morphology, the use of more suitable co-catalysts, processing MOFs into thin films, and optimizing reaction conditions.

Beyond photocatalysis, many photochemical processes involve electron–hole recombination. The next step is to extend the concept of excited-state dynamic structural twists to a broader range of photochemical processes. Additionally, our intention is to further diversify the applications of MOFs through discovering new dynamic structures.

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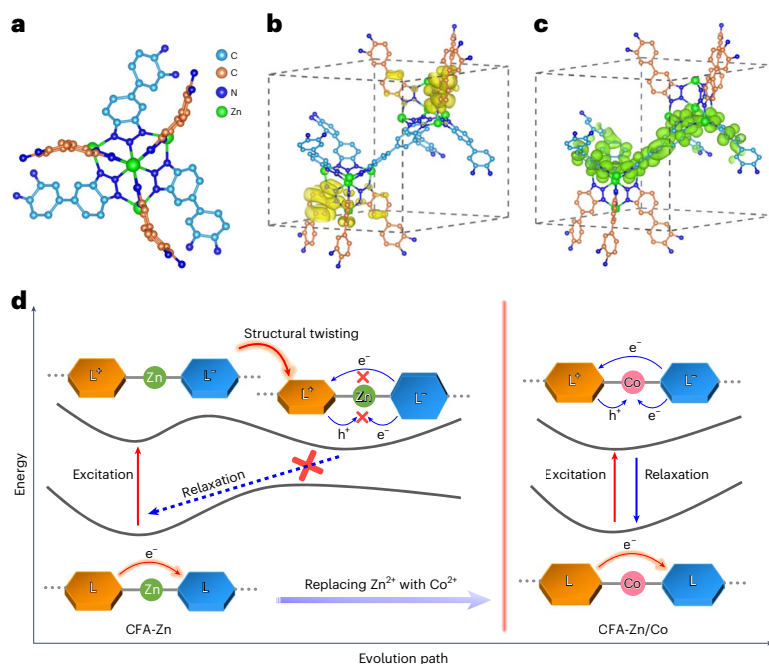
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## EXPERT OPINION

The authors have developed a novel and disruptive concept in heterogeneous photocatalysis using metal–organic frameworks (MOFs) towards the challenging solar-driven overall water splitting reaction. The newly reported MOF combines two crystallographically independent organic linkers that exhibit a dynamic excited-state

structural twist upon photoexcitation via a ligand-to-ligand charge transfer process. This situation favours long-lived charge-separated states and high photocatalytic activity. This work will provide new routes for the development of photoefficient MOFs. **An anonymous reviewer.**

## FIGURE



**Fig. 1 | The mechanism of the excited-state dynamic structural twist of a MOF in suppressing charge recombination.** **a**, The secondary building unit of the MOF, where the orange and light blue benzene rings represent crystallographically different linkers. X and H atoms have been omitted for clarity. **b, c**, Spatial distribution profiles of the (b) VBM and (c) CBM in a ground-state MOF single cell with an isosurface value of  $0.003 \text{ e}/\text{\AA}^3$ , demonstrating no electron cloud overlap between the VBM and CBM. Yellow bubbles and green bubbles represent the respective electron clouds. **d**, Schematic showing the mechanism of the long-lived charge-separated state in a MOF with Zn nodes (left), where the structural twist blocks electron relaxation; and the fast charge recombination in a MOF with Zn nodes that have been partially replaced by Co (right), where the absence of a structural twist leads to the rapid relaxation of excited electrons. Here,  $L^*$  and  $L^+$  represent the excited-state acceptors and donors of electrons, respectively. © 2024, Sun, K. et al.

## BEHIND THE PAPER

Our research team has been deeply engaged in MOF-based catalysis for over a decade<sup>5</sup>. Recently, we proposed the concept of biomimetic microenvironment modulation surrounding catalytic centres<sup>3</sup>. Our goal is to optimize particular microenvironments around catalytic sites to improve catalysis by learning from natural enzymes. MOF photocatalysis has been a central focus of our research for many years. However, achieving overall water splitting without a sacrificial agent remains a great challenge, with the rapid recombination of charge carriers being

a major obstacle. By closely examining natural photosynthesis, we identified that the dynamic flexibility of the natural components involved in charge transfer is crucial for achieving long-lived charge carriers. This insight led us to use a MOF that undergoes an excited-state dynamic structural twist for achieving efficient photocatalytic overall water splitting. Now, we are striving to explore the underlying mechanisms and optimize performance across various reactions through biomimetic microenvironment modulation. **K.S. & H.-L.J.**

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**This review summarizes progress and challenges in MOF photocatalysis.**

## FROM THE EDITOR

“Figuring out how molecules behave when they absorb light is tricky, but crucial for developing renewable energy chemistries. This work stood out to me because the excited-state molecular twisting observed here, while previously reported for model light-absorbers, rarely happens in actual solar-to-fuel reaction systems. Given the vast molecular design space offered by metal–organic frameworks, this work offers an exciting development for future photocatalysts.” Adam Weingarten, Senior Editor, *Nature Chemistry*.