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Coordination-driven assembly of a ferrocene-functionalized lead iodide framework with enhanced stability and charge transfer for photocatalytic CO₂-to-CH₃OH conversion†

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Hybrid lead halides are promising photocatalysts due to their high structural tunability and excellent photophysical properties, but their ionic structures suffer from instability in polar environments and suppressed charge transfer between lead halide units and organic components. Herein, we successfully incorporated a ferrocene-based light-harvesting antenna into a lead iodide framework by coordination-driven assembly. The π -conjugated Pb²⁺-carboxylate linkage affords synergistic interactions between [Pb₂I₂]²⁺ chains and ferrocene linkers, achieving broad visible absorption up to 612.7 nm and efficient ligand-to-metal charge transfer for spatial charge separation. This ultrastable framework combines strong visible-light absorption of ferrocene centers with excellent charge transport of lead halide units, achieving 6e[−] CO₂ photoreduction to CH₃OH coupled with ethanol oxidation. Mechanistic studies reveal that ferrocene photoexcitation followed by linker-to-metal charge transfer significantly enhances carrier accumulation, accelerating CH₃O* intermediate formation as indicated by *in situ* spectroscopy and theoretical calculations.

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Introduction

Chemical reduction of CO₂ to methanol (CH₃OH) is considered as the basis of the “methanol economy”, which is thermodynamically challenging and requires high energy input under industrially relevant conditions (*e.g.* high temperature and pressure).^{1–3} Mimicking the natural photosynthesis process, photocatalytic CO₂ reduction is one of the promising approaches for realizing a carbon neutral methanol economy.^{4–6} However, selectivity control in CO₂ photoreduction is extremely challenging, because the kinetically favorable 2e[−] reduction products (*i.e.* CO and HCOOH) often have high energy requirements for further protonation.^{7–12} Compared to other C₁ products, CH₃OH is more demanding owing to its liquid state for easy storage and transportation as well as its role as a precursor to many commodity chemicals and biodiesel.^{13–15} Photocatalytic reduction of CO₂ to CH₃OH requires the

simultaneous transfer of 6e[−] and 6H⁺ to the semiconductor surface, suppressing the undesired electron–hole annihilation.^{5,16} Therefore, it is of key importance to improve carrier accumulation on the semiconductor to realize CO₂-to-CH₃OH transformation, and only a few studies have reported high selectivity using environmentally friendly reductants.^{5,17,18} For example, carbon nitride (CN) decorated with carbon dots (^mCD) produces stoichiometric oxygen and CH₃OH from water and CO₂, which is largely ascribed to ^mCD extracting holes from CN and preventing the surface adsorption of CH₃OH.¹⁶

Lead halide hybrids are an emerging class of photocatalysts, spanning a variety of reactions including hydrogen production, CO₂ reduction and organic transformation.^{19–26} This class of semiconductors exhibits intriguing photophysical properties, such as tunable bandgaps, high light-absorption coefficients and excellent carrier transport characteristics.^{27–29} However, the vast majority of them are susceptible to degradation upon exposure to high-polarity protic molecules, ascribed to their soft ionically bound lattices.^{30,31} Up to now, their photocatalytic applications in CO₂ reduction are largely confined to low-polarity chemical conditions and limited to non-protic reducing products (*e.g.* CO and CH₄).³²

Our group focuses on the synthesis of lead halide frameworks based on carboxylate ligands as the organic component.³³ Unlike conventional hybrid halides featuring ionic structures, our lead halide frameworks exhibit remarkable structural stability with excellent photophysical properties.^{33–39} For

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† Electronic supplementary information (ESI) available: Experimental details of synthesis methods, additional XRD patterns, UV-vis absorption spectra, TGA spectra, UPS spectra, photocatalytic experiments, steady and transient state PL spectra, and computational methods for DFT. CCDC 2218953. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4sc08216h>

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example, adipate-intercalated layered lead halide frameworks ($[\text{Pb}_2\text{X}_2]^{2+}[\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2]^-$, $\text{X} = \text{F}^-/\text{Cl}^-/\text{Br}^-/\text{I}^-$) exhibit high chemical stability in aqueous solutions across a wide range of pH levels, as well as under aqueous boiling conditions.³³ This synthetic strategy enables lead halide frameworks to achieve CO_2 photoreduction to CO using water vapor as well as photocatalytic overall water splitting without any sacrificial agent.^{40,41} However, their photocatalytic efficiency remains limited due to the spatial separation of lead halide units by photochemically “inert” organocarboxylates, which often restricts visible-light absorption.^{40,41} Although unexplored in the literature, the integration of light-harvesting ferrocene-based linkers into lead iodide frameworks will be a promising photocatalysis platform, offering both strong photon absorption and enhanced carrier accumulation.

Ferrocene (Fc)-functionalized moieties exhibit outstanding visible-light absorption and charge transfer characteristics, making them excellent organometallic components in optoelectronic applications.^{42,43} However, there have been very few reports on Fc-functionalized lead halide hybrids, and the ionic bonding between lead halide units and Fc ligands hinders intrinsic electron transfer and effective charge separation for photocatalysis.^{44,45} Recently, Dong and colleagues demonstrated that grafting ferrocenecarboxylic acid (FCA) onto CsPbBr_3 quantum dots substantially enhances photocatalytic efficiency for CO_2 -to-CO conversion, facilitating hot electron transfer from the FCA to the quantum dots.⁴⁶ This improvement is attributed

to the coordination bonds formed between these two components.⁴⁶ However, the coordination-driven assembly of Fc-functionalized moieties and lead halide sublattices to afford an intrinsic framework-type structure remains an outstanding challenge, representing a significant advance for improving both light absorption and charge transfer in lead halide photocatalysis.

Herein, we report a robust lead iodide framework possessing 1D linear $[\text{Pb}_2\text{I}_2]^{2+}$ chains, which are bridged by $[\text{Pb}_2\text{O}_2]$ clusters into inorganic lamellar units. The inorganic sheets are coordinatively decorated with interlamellar 1,1'-ferrocenedicarboxylates (Fcdc^{2-}) as light-harvesting chromophores, stacked by van der Waals interactions. In contrast to Fc-based perovskite ($(\text{FMTMA})\text{PbI}_3$) with non-covalent interactions between the Fc moieties and lead halide building blocks, the formation of π -conjugated Pb^{2+} -carboxylate coordination in our framework results in enhanced carrier delocalization and carrier transport. The material exhibits a broad visible-light wavelength coverage with an indirect semiconductive bandgap of ~ 1.92 eV and efficient photoinduced charge transfer from Fcdc^{2-} to the 1D $[\text{Pb}_2\text{I}_2]^{2+}$ chains. The favorable ligand-to-metal charge transfer (LMCT) process greatly improves photo-generated charge separation, as thoroughly investigated by surface photovoltage spectroscopy, Hall effect measurement and density functional theory (DFT) calculations. Combining the ultrastable nature and the intriguing carrier dynamics, the lead iodide framework achieves photoreduction of CO_2 to

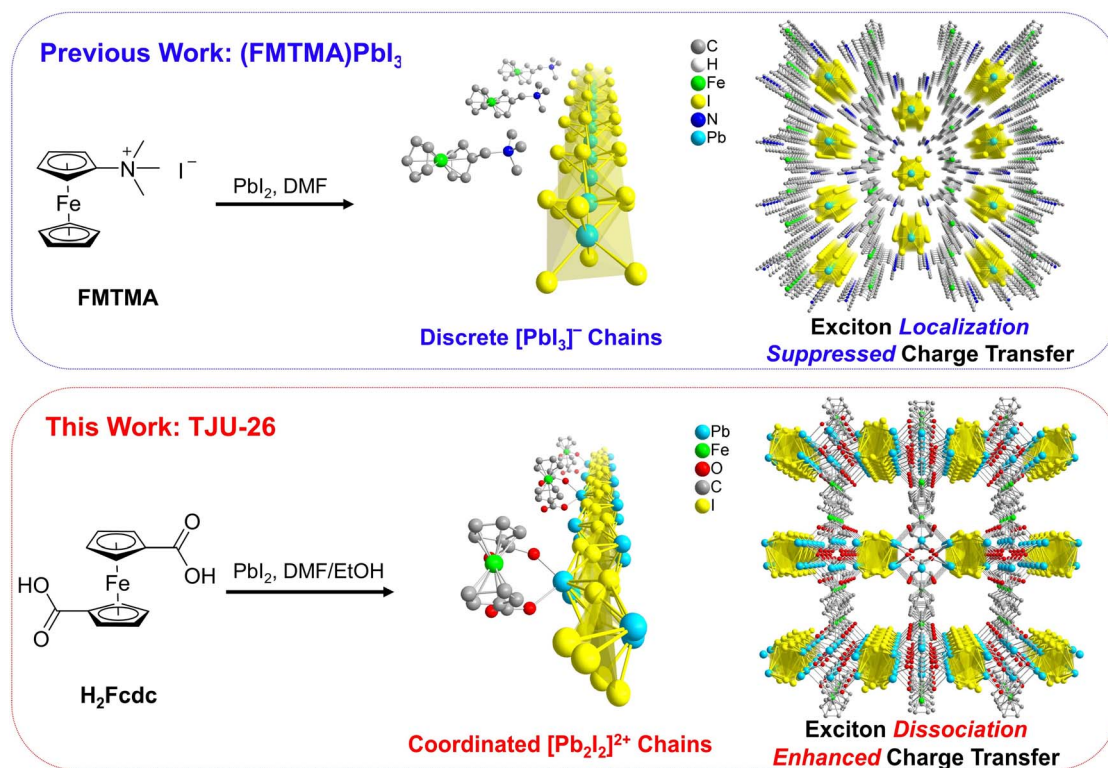


Fig. 1 (Top) Synthetic scheme and crystallographic view of $(\text{FMTMA})\text{PbI}_3$, including a single $[\text{PbI}_3]^-$ chain with FMTMA^+ cations and the overall structure of $(\text{FMTMA})\text{PbI}_3$. (Bottom) Synthetic scheme and crystallographic views of TJU-26, including a single $[\text{Pb}_2\text{I}_2]^{2+}$ chain coordinated with Fcdc^{2-} ligands and the overall structure of TJU-26.



CH₃OH with exceptionally high selectivity, by using ethanol (EtOH) as an environmentally benign electron donor and solvent.

Results and discussion

Synthesis and crystal structures

Conventional Fc-functionalized lead iodide perovskite, (FMTMA)PbI₃ (FMTMA = ferrocenylmethyltrimethylammonium), was synthesized following a previously established procedure.⁴⁵ This compound exhibits a typical ABX₃-type perovskite structure, consisting of a hexagonal arrangement of infinite linear chains of face-sharing PbI₆ octahedra along the *c* axis, with the FMTMA cations separating the chains through non-covalent electrostatic interactions (Fig. 1 top). In contrast, our ferrocene-functionalized lead iodide framework was synthesized by solvothermal reactions between PbI₂ and 1,1'-ferrocenedicarboxylic acid (H₂Fcdc) in DMF/EtOH, forming reddish-brown platelike crystals of [Pb₂I₂]²⁺[PbO][Fcdc²⁻], (TJU-26, TJU = Tongji University) (Fig. 1 bottom and S1†). X-ray crystallography reveals that the framework consists of an array of unidimensional linear [Pb₂I₂]²⁺ chains propagating along the *b*-axis (Fig. S2†). All of the iodide species are μ₃-bridged among Pb²⁺ centers with Pb–I bond lengths between 3.287(1) and 3.590(1) Å. The iodo-plumbate chains are connected by square [Pb₂O₂] units, forming lead oxiodide inorganic layers along the *ab* plane (Fig. S2†). Moreover, the Fcdc²⁻ ligands coordinatively decorate the Pb²⁺ centers to form a layered hybrid architecture (Fig. S3†). Moreover, the strong coordination bonding between the Pb²⁺ centers in the [Pb₂I₂]²⁺ chains and the carboxylate groups in the Fcdc²⁻

ligands is evidenced by the short Pb–O bond distances of 2.276–2.430 Å, which are significantly lower than the Pb–O distances of 2.753–2.872 Å observed between neutral [Pb₂O₂] units and Fcdc²⁻ ligands (Fig. S4†). Using carboxylate as the coordinating ligand, rather than conventional Fc-based organoammonium, facilitates an essential transition from an ionically bound lead halide perovskite to a lead halide framework, affording high structural stability and efficient charge-transfer behavior between the [Pb₂I₂]²⁺ chains and the Fcdc²⁻ ligands, as discussed in detail later.

A good match between experimental powder X-ray diffraction (PXRD) and the simulated pattern from the single-crystal data confirms the high yield and good phase purity of TJU-26 and (FMTMA)PbI₃ (Fig. 2a and S5†). Fourier transform infrared (FT-IR) spectra suggest the presence and deprotonation of Fcdc²⁻ in TJU-26 (Fig. S6†). Stability measurements show that the as-synthesized (FMTMA)PbI₃ crystals rapidly dissolve in polar organic solvents (*e.g.* DMF and DMSO). However, the as-synthesized TJU-26 is stable in these solvents for at least 24 h with no obvious loss in both crystallinity and mass balance, evidencing the high chemical stability of the coordination network (Fig. 2a). Thermogravimetric analysis (TGA) and *ex situ* thermogravimetric analysis (TGA) and *ex situ* thermogravimetric analysis (TGA) show high thermal stability up to 220 °C for TJU-26, higher than 200 °C for (FMTMA)PbI₃ (Fig. S7 and S8†). Moreover, the photostability of TJU-26 was examined by continuous irradiation with AM 1.5G simulated sunlight (42 mW cm⁻²) for 48 h at room temperature. The overall stability of TJU-26 remained largely unaffected as confirmed by PXRD, while the slight discrepancy in absorption spectra is likely due to the partial surface modification during prolonged light irradiation (Fig. 2b and S9†). In contrast, a new diffraction peak

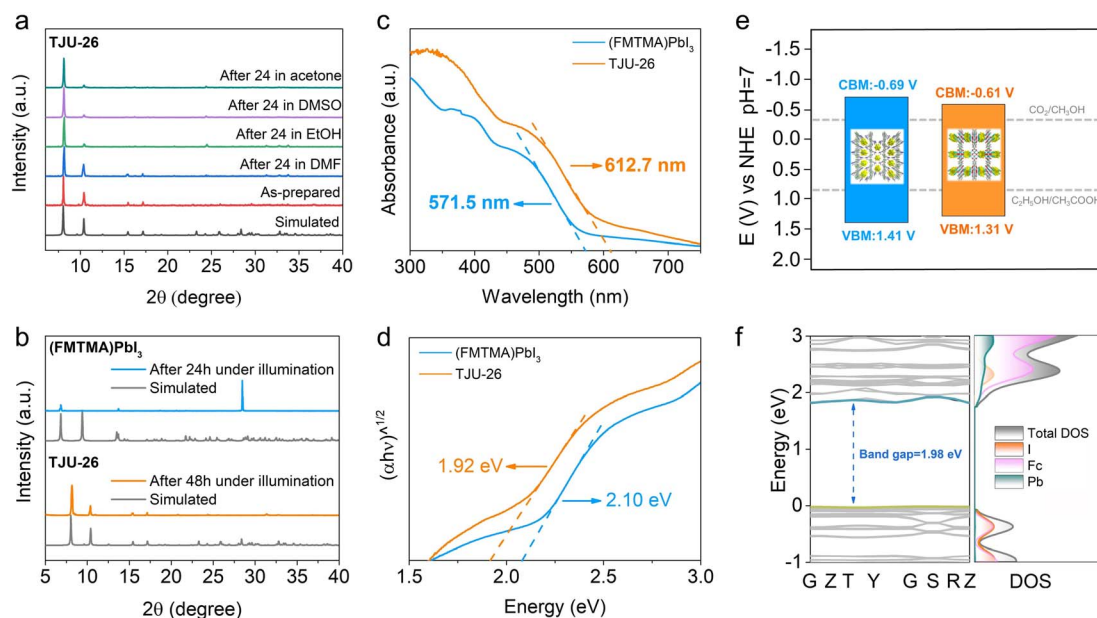


Fig. 2 (a) PXRD patterns of TJU-26 before and after 24 h treatment in different organic solvents. (b) The PXRD patterns of TJU-26 and (FMTMA)PbI₃ after light irradiation (300 W Xe lamp, AM 1.5G) for 48 h and 24 h, respectively. (c) Normalized UV-vis diffuse reflectance spectroscopy of TJU-26 and (FMTMA)PbI₃. (d) Tauc plots of TJU-26 and (FMTMA)PbI₃. (e) Band alignment of TJU-26 and (FMTMA)PbI₃. (f) Calculated band structure and DOS of TJU-26.

(28.5°) in PXRD was clearly observed for (FMTMA)PbI₃ after continuous irradiation for 24 h, suggesting the decomposition of the perovskite structure (Fig. 2b). Overall, the stability tests suggest that TJU-26 is a robust compound to perform photocatalysis in high-polarity protic solvents.

Electronic band structure

Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy shows that TJU-26 has a broad visible absorption range with the absorption edge extending to 612.7 nm, superior to all of our previously reported lead halide frameworks (Fig. 2c).³³ The band gap energy (E_g) of TJU-26 was estimated to be 1.92 eV using the Tauc plot method (Fig. 2d). This enhancement in visible light absorption is attributed to the incorporation of the light-harvesting Fcdc²⁻ ligand, which substantially improves phonon absorption across the solar spectrum. The ferrocene-functionalized perovskite, (FMTMA)PbI₃, exhibits a narrower visible absorption range with an absorption edge of 571.5 nm and a larger E_g of 2.10 eV (Fig. 2c and d). The reduced E_g of TJU-26 suggests that the formation of Pb²⁺-carboxylate coordination bonds between the Fcdc²⁻ and the lead iodide chains effectively enhances the conjugation of the framework.⁴⁷ In addition, ultraviolet photoelectron spectroscopy (UPS) revealed that the valence band (VB) potentials (vs. the vacuum level) of TJU-26 and (FMTMA)PbI₃ were −5.81 eV (+1.31 V vs. NHE pH 7) and −5.91 eV (+1.41 V vs. NHE pH 7), respectively (Fig. S10 and S11†). Their corresponding conduction band (CB) potentials (vs. the vacuum level) were −3.89 eV (−0.61 V vs. NHE pH 7) and −3.81 eV (−0.69 V vs. NHE pH 7), respectively. These values indicate that both TJU-26 and (FMTMA)PbI₃ are thermodynamically capable of photocatalytic CO₂ reduction coupled with EtOH oxidation (Fig. 2e).

DFT calculations suggest the calculated bandgap of TJU-26 to be 1.98 eV, close to the experimental value of 1.92 eV and again confirming its semiconductive nature (Fig. 2f). The total density of states (DOS) and the projected density of states (pDOS) on the Pb, I and Fcdc²⁻ ligands indicate that the valence band maximum (VBM) is dominated by I 5p orbitals, while Pb 6p orbitals largely contribute to the conduction band minimum (CBM) (Fig. 2f). The significant roles of Pb and I in frontier orbitals are analogous to the conventional hybrid lead halides, evidencing their contributions to carrier formation for photocatalysis.^{48,49} Meanwhile, owing to the Pb²⁺-carboxylate coordination motifs, the Fcdc²⁻ linkers are involved in frontier orbitals as well, which agrees with the potential ligand-to-metal charge transfer (Fig. 2f).⁵⁰

Charge transport dynamics

Since the incorporation of the light-harvesting chromophore largely extended the visible-light absorption of TJU-26, it is important to investigate the LMCT process after the photoexcitation of the Fcdc²⁻ linkers and the e[−]-h⁺ separation. First, from the structural point of view, the π -conjugation between the cyclopentadiene ring and the carboxylate in the Fcdc²⁻ ligands allows for the transfer of delocalized electrons from Fc moieties to the soft [Pb₂I₂] chains, unlike ionic Fc-based perovskites

(Fig. 1).⁴⁵ Following this, the LMCT is evidenced by the substantial photoluminescence decrease of Fcdc²⁻ after incorporation into TJU-26, which exhibits a strong emission band at 379 nm for the free Fcdc²⁻ ligands (Fig. S12 and S13†). Meanwhile, TJU-26 shows largely quenched but broad photoluminescence ranging from 380 to 700 nm, with an average lifetime of 150.8 ns based on time-resolved photoluminescence (tr-PL) decay (Fig. 3a). The best fit of the decay provides a bi-exponential function with time constants of a long carrier lifetime of 601.7 ns and a short lifetime of 46.7 ns. Meanwhile, the tr-PL spectra of H₂Fcdc and (FMTMA)PbI₃ show that the average lifetimes are lower than that of TJU-26, with 98.4 ns for H₂Fcdc and 109.3 ns for (FMTMA)PbI₃, respectively (Fig. 3a). The higher PL lifetime of TJU-26 again supports the claim that the Pb²⁺-carboxylate coordination motifs between the conjugated Fcdc²⁻ ligand and the Pb²⁺ center are more favorable for the LMCT process. Indeed, DOS calculations show the contribution of the Fcdc²⁻ ligands and the Pb 6p orbitals to the VBM and CBM, respectively, agreeing with the claim of the LMCT process (Fig. 2f). In addition, the presence of the LMCT process in TJU-26 was confirmed by X-ray photoelectron spectroscopy (XPS). In the high-resolution XPS spectra of Fe 2p, the two peaks located at 710.6 eV and 723.1 eV are ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively.⁵¹ Meanwhile, a series of XPS characteristic peaks of Fe³⁺ (714.7 eV for Fe³⁺ 2p_{3/2} and 728.1 eV for Fe³⁺ 2p_{1/2}) were also observed upon irradiation, which confirms the charge transfer process from the Fcdc²⁻ ligands to the Pb²⁺ sites (Fig. S14†).⁵²

Importantly, LMCT is known to facilitate the separation and transport of photogenerated carriers, and surface photovoltage (SPV) spectroscopy is an important approach for investigating charge separation.⁵³ The photovoltage (PV) onset of TJU-26 occurs at 2.86 eV (433 nm), and the maximum voltage of 819 mV is observed at 3.27 eV (379 nm) (Fig. 3b). Based on the band structure of TJU-26, the PV response is determined to be the charge separation of the band states. Given the SPV measurement of the TJU-26 film on FTO glass (see the Experimental section in the ESI†), the maximum theoretical photovoltage for the FTO/TJU-26 contact is 990 mV. Therefore, the experimental photovoltage of TJU-26 reaches ~83% of this limit.^{54,55} However, the ionically bound Fc-based perovskite, (FMTMA)PbI₃, exhibits a decreased maximum PV of 194 mV, corresponding to approximately 20% of the theoretical maximum PC (Fig. 3b). Despite the resemblance in SPV spectra, the nearly fourfold higher PV of TJU-26 indicates a significantly greater charge separation efficiency that is attributed to the efficient LMCT in TJU-26. Enhanced charge separation in TJU-26 is further supported by (photo)electrochemical studies. The photocurrent signal of TJU-26 is substantially higher than that of (FMTMA)PbI₃, reflecting improved electron-hole separation efficiency (Fig. S16†).⁵⁶ In addition, the smaller radius observed in the electrochemical impedance spectral (EIS) plots for TJU-26 implies a lower electron transfer resistance (Fig. S17†). The interfacial charge transfer resistance (R_{ct}) for TJU-26 is 3.6 k Ω , significantly lower than the 24.9 k Ω measured for (FMTMA)PbI₃, suggesting superior electron mobility in TJU-26.⁵⁷

Hall effect measurements at room temperature reveal that TJU-26 exhibits n-type semiconductor behavior, with a carrier



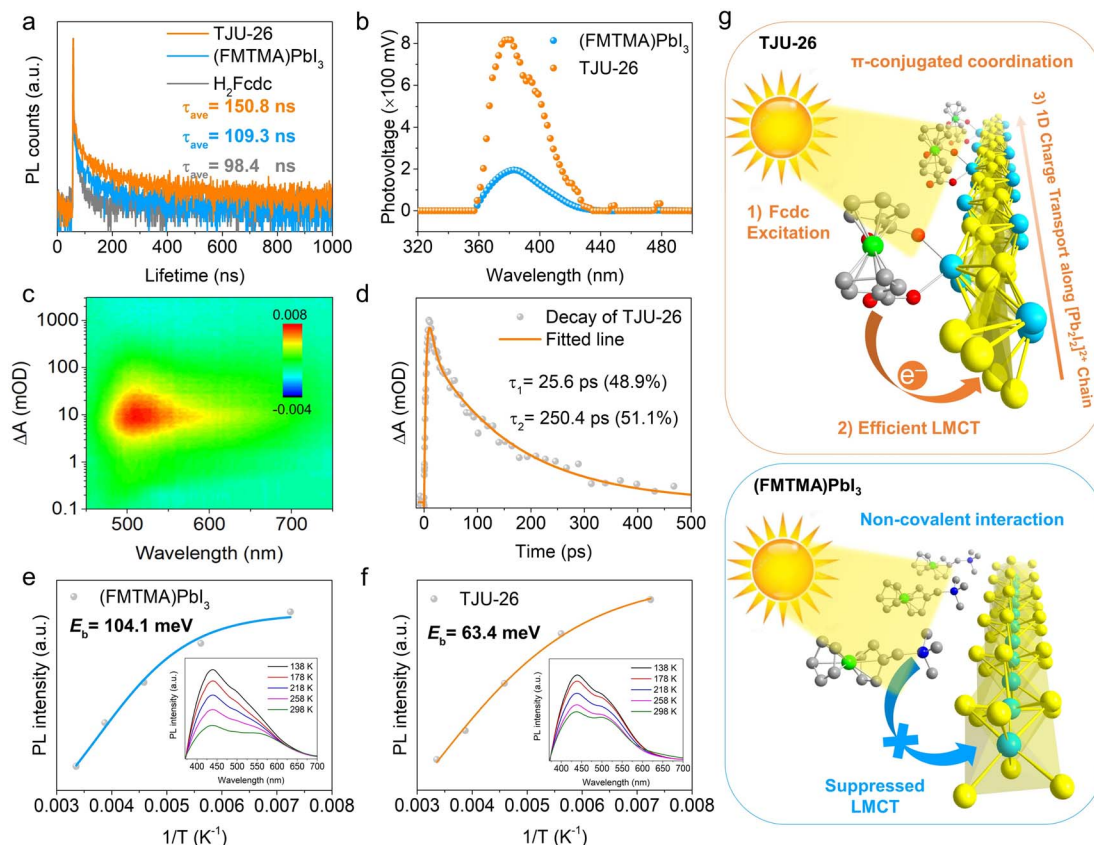


Fig. 3 (a) Photoluminescence decay of H₂Fcdc, (FMTMA)PbI₃ and TJU-26 at room temperature. (b) SPV spectra of TJU-26 and (FMTMA)PbI₃. (c) Two-dimensional pseudo-color TA plot of TJU-26. (d) TA kinetics of TJU-26. (e) Extracted exciton binding energies of TJU-26. (Inset) Temperature-dependent PL spectra of TJU-26 with an excitation wavelength of 355 nm. (f) Extracted exciton binding energies of (FMTMA)PbI₃. (Inset) Temperature-dependent PL spectra of (FMTMA)PbI₃ with an excitation wavelength of 350 nm. (g) Schematic presentation showing the photoexcitation, photoinduced LMCT and carrier transport of TJU-26 (left) and the suppressed photoinduced LMCT in (FMTMA)PbI₃ (right).

concentration of $9.8 \times 10^{13} \text{ cm}^{-3}$ and an estimated carrier mobility of $\sim 0.114 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These values are comparable to those of many benchmark 3D lead halide perovskites and several orders of magnitude higher than those observed for 1D (FMTMA)PbI₃ ($4.1 \times 10^{10} \text{ cm}^{-3}$ and $0.032 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{28,29} This enhancement suggests that the incorporation of light-harvesting Fcdc²⁻ ligands improves visible-light photon absorption in TJU-26, followed by an LMCT process that further enhances charge separation. In addition, the average carrier diffusion lengths of TJU-26 and (FMTMA)PbI₃ were determined to be 0.21 μm and 0.09 μm , respectively, based on the equation

$$L_D = \left(\frac{k_B T}{e} \times \mu \times \tau \right)^{1/2} \quad (1)$$

where k_B is Boltzmann's constant, T is the temperature, e is the electron charge, μ is the Hall mobility, and τ is the carrier lifetime. Moreover, the effective masses of charge carriers in TJU-26 were calculated to be $2.10 m_0$ for electrons (m_e^*) and $0.51 m_0$ for holes (m_h^*), respectively. It is well established that small carrier effective masses contribute to high carrier mobility and long carrier diffusion lengths.⁵⁸

To obtain detailed insights into the charge carrier dynamics of TJU-26 under light irradiation, femtosecond transient

absorption (fs-TA) spectroscopy was performed upon 320 nm excitation. The pseudo-color fs-TA spectra of TJU-26 exhibit a positive signal across the 450–800 nm range, with a maximum at 515 nm (Fig. 3c). This signal is attributed to the absorption from photoinduced electron transfer and directly reveals the process of charge separation within 1D lead iodide chains under light exposure.⁵⁹ This signal reaches its maximum value at ~ 10 ps at 515 nm, suggesting a high rate of charge separation (Fig. S18†). However, the peak at 515 nm rapidly weakens around 50 ps, with a concomitant appearance of a new peak at 667 nm, indicating a change in the interactions between photogenerated electrons and holes (Fig. S18†).⁶⁰ This new observation is attributed to electron transfer from the Fcdc²⁻ ligand to the [Pb₂I₂]²⁺ SBUs via the Pb²⁺-carboxylate linkage under photoexcitation, which facilitates spatial charge separation and transport. Analysis of the recovery kinetics at 515 nm in the TA spectra shows that the decay of TJU-26 follows a biexponential function with two time constants, $\tau_1 = 25.6$ ps and $\tau_2 = 250.4$ ps (Fig. 3d), resulting in a long average lifetime of 122.6 ps. These findings indicate that the charge transfer between the Fcdc²⁻ ligand and the lead halide structural unit probably delays TA decay kinetics, thereby suppressing electron-hole recombination.⁶¹

To further investigate the exciton dissociation behaviors of TJU-26 and (FMTMA)PbI₃, temperature-dependent photoluminescence (PL) measurements were conducted to determine their exciton binding energies (E_b) (Fig. 3e and f). The PL intensities of both materials decreased as the temperature increased, primarily due to thermally activated nonradiative recombination processes.⁶² The E_b was estimated by combining integrated PL intensity with temperature, using the following equation:

$$I(T) = \frac{I_0}{1 + Ae^{-E_b/k_B T}} \quad (2)$$

where I_0 is the PL intensity at 0 K, A is a proportional constant, and k_B is the Boltzmann constant. By fitting the experimental data, the E_b values of TJU-26 and (FMTMA)PbI₃ were determined to be 63.4 meV and 104.1 meV, respectively (Fig. 3e and f). TJU-26 exhibited a lower E_b than (FMTMA)PbI₃, suggesting the high tendency of electrons and hole dissociation into free carriers in TJU-26.⁶³ These photophysical studies indicate that the coordination linkage between Fcdc²⁻ and Pb²⁺ centers facilitates an effective LMCT process, which not only enhances carrier transport but also promotes exciton dissociation within the [Pb₂I₂]²⁺ chains, making TJU-26 a promising candidate for multi-e⁻ CO₂ photoreduction (Fig. 3g).

Photocatalytic CO₂-to-CH₃OH conversion

Given the suitable band positions and excellent carrier separation/transport of TJU-26, CO₂ photoreduction was studied by introducing 20 mg as-synthesized TJU-26 into a sealed reaction system containing 10 mL EtOH and 1 atm CO₂. No additional photosensitizer, metal co-catalyst or sacrificial reducing agent was necessary for this photocatalytic system. EtOH functions not only as a donor scavenger, accepting photogenerated holes, but also as an environmentally benign solvent. Both ¹H nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC) have been employed to quantitatively identify the reduction products. Upon AM 1.5G simulated illumination, TJU-26 steadily catalyzed CO₂ reduction to produce CH₃OH as the major product over a time span of 4 h (Fig. 4a and S19†). A linear increment in the CH₃OH yields was observed and the average CH₃OH evolution rate was determined to be 26.31 μmol h⁻¹ g⁻¹, while trace amounts of CO (0.14 μmol h⁻¹ g⁻¹) and CH₄ (1.60 μmol h⁻¹ g⁻¹) were detected as well (Fig. 4a). These values correspond to photocatalytic selectivities of 92.3% (electron basis) and 93.7% (product basis) for CO₂-to-CH₃OH transformation, which are among the highest reported values for hybrid lead halides (Table S2†). Moreover, the CO₂ photoreduction performance of TJU-26 is comparable to that of benchmark CO₂-to-CH₃OH photocatalysts, such as carbon dot-based photocatalysts (^mCD) (13.9 μmol h⁻¹ g⁻¹) and Bi₁₉Br₃S₂₇ (0.62 μmol h⁻¹ g⁻¹) (Table S3†).^{7,16}

Control experiments conducted in the absence of TJU-26, light, or CO₂ yielded no methanol, confirming that the methanol formation results from the CO₂ reduction reaction catalyzed by TJU-26 (Fig. 4b). To further confirm the origin of the carbon source, a control photocatalytic experiment was carried

out using ¹³C isotopically labelled CO₂. The chemical shift signal peak at 48.6 ppm (¹³CH₃OH) was clearly observed by ¹³C NMR spectroscopy. Meanwhile, no peak was observed at 48.6 ppm using ¹²CO₂ under identical reaction conditions, demonstrating that the CH₃OH product arises from the reduction of CO₂ instead of other carbon sources (Fig. 4c). In order to confirm the multi-electron CO₂ reduction process, the kinetically favorable 2e⁻ reduced product (*i.e.* formic acid, HCOOH) is employed as the precursor. Photocatalysis in a closed reaction system containing 40 mg TJU-26 and 20 μL formic acid in 8 mL EtOH without CO₂ produces CH₃OH as the major product at an evolution rate of 29.54 μmol h⁻¹ g⁻¹ (Fig. S20†). This set of experiments confirm that the populated carrier accumulation nature of TJU-26 enables the further reduction of 2e⁻ intermediates to afford the final product of CH₃OH. Moreover, we have performed control photocatalysis experiments to exclude the presence of ethanol, using sodium sulfite as the hole scavenger in aqueous solution instead. In this system, the evolution rates of CH₃OH, CH₄, and CO were measured to be 10.53 μmol h⁻¹ g⁻¹, 0.67 μmol h⁻¹ g⁻¹, and 6.34 μmol h⁻¹ g⁻¹, respectively (Fig. S21†). These results provide further evidence that methanol is derived from the photoreduction of CO₂, rather than from the decomposition of ethanol.

The wavelength-dependent apparent quantum efficiencies (AQEs) were measured to be 0.41% at 400 nm (±15 nm), 0.35% at 420 nm (±15 nm), 0.24% at 500 nm (±15 nm) and 0.22% at 550 nm (±15 nm) (Fig. 4d). The trend is consistent with the UV-vis absorption of TJU-26, implying an intrinsic photo-driven catalytic process. In control experiments, (FMTMA)PbI₃ was measured under identical photocatalytic conditions, resulting in CO₂ reduction products of CO and CH₄ with evolution rates of 9.83 μmol h⁻¹ g⁻¹ and 2.21 μmol h⁻¹ g⁻¹, respectively (Fig. 4b). The significantly enhanced photocatalytic CO₂ reduction performance of TJU-26 again confirms the essential role of the π-conjugated coordination linkage between Fcdc²⁻ ligands and [Pb₂I₂]²⁺ chains in facilitating charge separation and transport (Fig. 3g).

The long-term photocatalytic stability of TJU-26 was studied by performing photocatalysis under continuous AM 1.5G illumination for a total of 16 h, with evacuation and CO₂ refilling every 4 h (Fig. 4e). The photocatalyst retained over 93% of the initial CO₂ photoreduction activity for the next three runs, showing the excellent durability of TJU-26 under the photocatalytic conditions. Moreover, PXRD, UV-vis and FTIR spectroscopy synergistically indicate that TJU-26 largely retains its structural integrity after photocatalysis (Fig. S22–S24†). Indeed, a negligible amount of Pb²⁺ leaching was noticed in the solution after the photocatalytic reaction (1.12 ppm by inductively-coupled plasma optical emission spectroscopy, ICP-OES). Meanwhile, the role of EtOH as an electron donor was confirmed by the presence of acetic acid (CH₃COOH) as the oxidized product by ¹H NMR, which was performed by a continuous photocatalytic reaction for 12 h (Fig. 4f). The quantitative characterization of acetic acid was performed by using DMSO as the internal standard, corresponding to an evolution rate of 32.2 μmol h⁻¹ g⁻¹ (Fig. S25†). This value accounts for ~83% of the theoretical yield for the oxidation



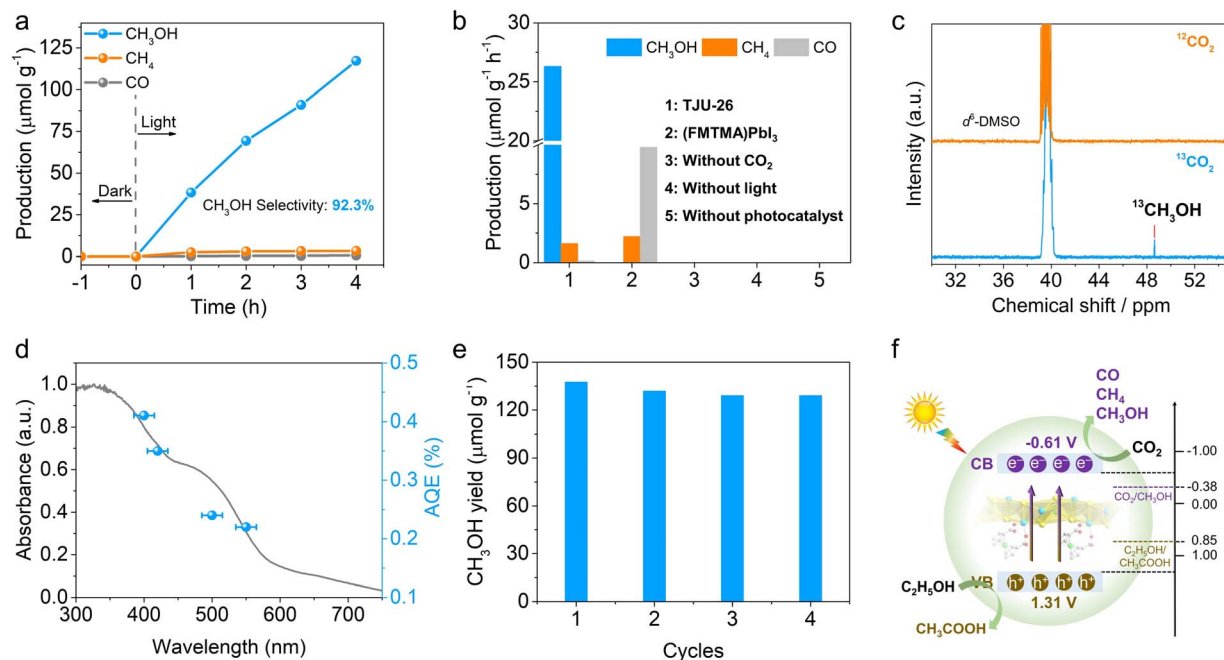
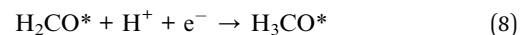
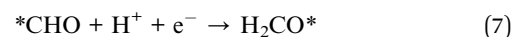
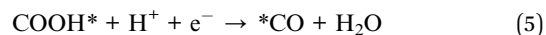


Fig. 4 (a) Time courses of CH₃OH, CH₄ and CO evolution for photocatalytic CO₂ reduction by TJU-26 in EtOH (AM1.5G simulated sunlight). (b) The control experiments of photocatalytic CO₂ reduction performance over TJU-26 and (FMTMA)PbI₃. (c) ¹³C NMR results of ¹³CH₃OH produced over TJU-26 from the ¹³CO₂ isotope experiment. (d) Wavelength-dependent AQEs of photocatalytic CO₂ reduction on TJU-26. Error bars represent the deviations of monochromatic light wavelengths. (e) Time courses of CH₃OH production over 20 mg of TJU-26 in 10 mL of EtOH for four consecutive cycles. (f) Schematic diagram for photocatalytic CO₂ reduction by TJU-26.

product, demonstrating that CH₃CH₂OH-to-CH₃COOH oxidation is the major coupling reaction in CO₂ photoreduction. Notably, coupling CO₂ photoreduction with alcohol oxidation has emerged as an appealing approach for synergistic utilization of photogenerated electrons and holes, offering an advantage over the conventional use of hole scavengers such as triethylamine (TEA).⁶⁴

Photocatalytic mechanism

To understand the photoreaction mechanism on TJU-26, the surface species evolved in the reaction were monitored by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Fig. 5a). First, during the DRIFT studies, no intermediate was observed in N₂ or in the dark under identical conditions, suggesting the CO₂ photoreduction process. When performing CO₂ catalysis with light irradiation, a prominent band at 1620 cm⁻¹ for carboxyl stretching is gradually observed with the irradiation time increasing from 0 to 60 min. This peak suggests the presence of *COOH species as one of the intermediates.^{65,66} The *CHO intermediate with a characteristic band at 1070 cm⁻¹ is noticed as well, implying the possible protonation of COOH* to afford *CO and the follow-up proton transfer to form *CHO.⁶⁷ More importantly, the concomitant absorption bands at 1040 cm⁻¹ and 1160 cm⁻¹ are clearly observed, suggesting the presence of H₃CO*, which is one of the key intermediates during the CO₂-to-CH₃OH transformation.^{7,68} According to the above results, it is speculated that the most likely reduction pathway could be as follows:



where “*” represents the corresponding adsorption sites on the surface of the photocatalyst.

Following this, we have explored the active sites for photocatalytic CO₂ reduction on TJU-26 by quasi *in situ* XPS spectroscopy. Under light irradiation, the I 3d peak shifted to higher binding energy, indicating a decrease in the electron density around the I site (Fig. S26†).⁶⁹ Meanwhile, we have observed characteristic peaks of both Fe²⁺ and Fe³⁺ in the high-resolution Fe 2p spectra, and the percentage of Fe³⁺ increased substantially under light irradiation, which was attributed to the charge transfer from the Fcdc²⁻ ligands to the Pb²⁺ sites through the Pb²⁺-carboxylate coordination bridge (Fig. S14 and S15†).⁵² Indeed, the Pb 4f peak shifted to lower binding energy, indicating that the electron density around the Pb²⁺ site in TJU-26 increased after light irradiation (Fig. S27†).⁷⁰ Overall, the

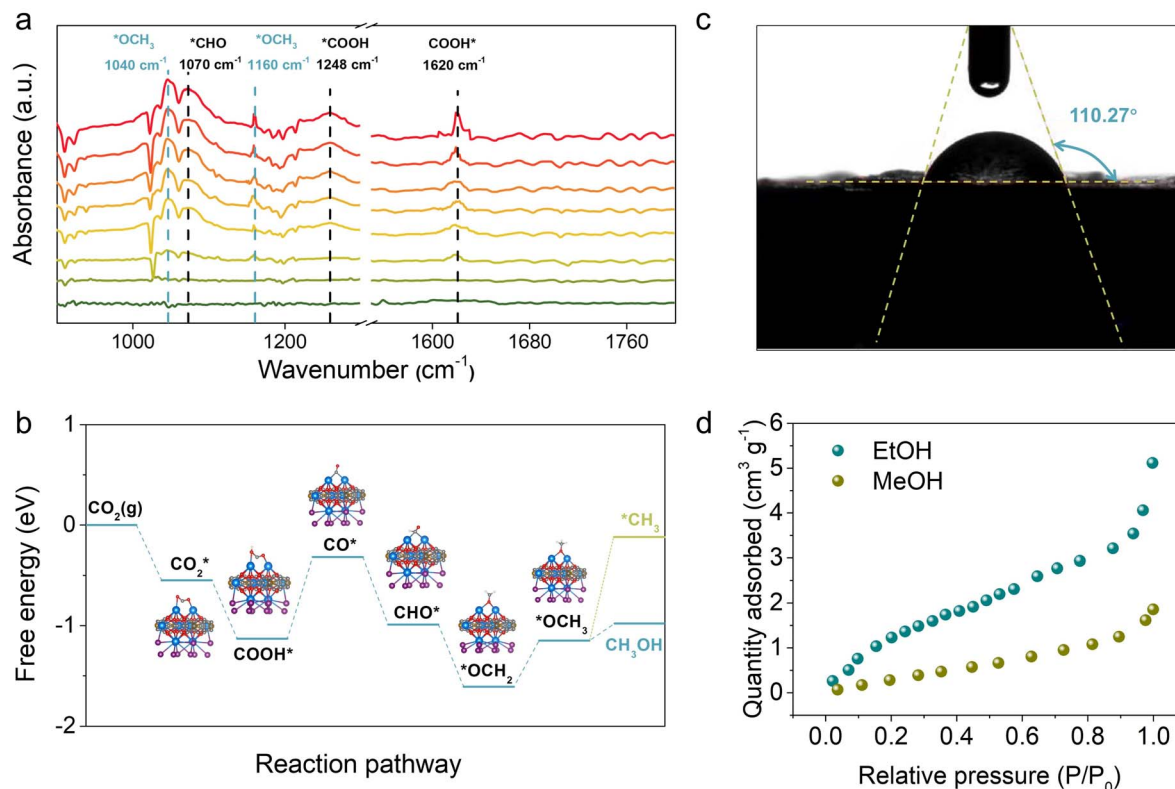


Fig. 5 (a) *In situ* DRIFTS spectra for the photocatalytic CO₂ reduction process by TJU-26. (b) Free energy diagram of photocatalytic CO₂-to-CH₃OH transformation on the (001) facet of TJU-26. (c) Contact angle measurement of TJU-26 with water. (d) Vapor adsorption isotherms of TJU-26 at 298 K.

increase in the electron density of the Pb²⁺ sites in TJU-26 facilitates CO₂ adsorption and activation.

To further understand the reaction mechanism, we have performed Gibbs free energy calculations using the (001) facet as the representative surface of TJU-26 to model the possible reaction pathways involved in the CO₂-to-CH₃OH process. First, the CO₂ adsorption calculations indicate that the CO₂ adsorption and activation on TJU-26 are thermodynamically favorable (Fig. 5b). Importantly, the formation of the COOH^{*} intermediate (eqn (4)) is found to be a spontaneous process on TJU-26, which is often the rate-determining step in many previous studies.⁷ In this exothermic step, the oxygens of the COOH^{*} species preferentially bind with two adjacent Pb²⁺ sites in a bidentate manner, resulting from the suitable Pb...Pb distance of 3.691 Å in the lead oxyiodide layers. To note, both Pb²⁺ centers originate from the [Pb₂I₂]²⁺ chains instead of [Pb₂O₂] clusters, verifying that the iodoplumbate species indeed serve as photocatalytically active sites. The protonation of ^{*}COOH to produce ^{*}CO by TJU-26 has a low free-energy barrier of 0.81 eV to form the C-anchored ^{*}CO intermediate. This reaction pathway is further confirmed by a control experiment using formic acid instead of CO₂ as the precursor to produce CH₃OH at an evolution rate of 29.54 μmol h⁻¹ g⁻¹. Since the carbon of ^{*}CO has a contact distance of 2.175 Å with one Pb²⁺ site, the moderate adsorption strength of ^{*}CO tends to accept a proton-electron pair to form ^{*}CHO (eqn (6)) instead of CO

desorption as the by-product (evolution rate of 0.14 μmol g⁻¹ h⁻¹). The thermodynamically favorable process for the conversion of ^{*}CO to ^{*}CHO is supported by both DFT calculations and the observed ^{*}CHO species (1070 cm⁻¹) in the aforementioned *in situ* DRIFT studies (Fig. 5a). Following this, DFT calculations suggest that the reaction undergoes the formyl pathway, where the addition of another electron-hole pair leads to the formation of H₂CO^{*} through an exothermic process (eqn (7)), thanks to the bidentate binding motif with dual Pb²⁺ centers. This suggests the important transition from C-anchored ^{*}CHO to O-anchored H₂CO^{*} on TJU-26 (Fig. 5b). Subsequently, H₂CO^{*} accepts one more electron-hole pair to form CH₃O^{*}, which agrees with the *in situ* DRIFT observations. Although the hydrogenation of ^{*}OCH₃ to CH₃OH is an uphill process, the free-energy change for this step is much smaller than that for the conversion of ^{*}OCH₃ to ^{*}CH₃ via the acceptance of two e⁻/H⁺ pairs (Fig. 5b). This effectively rules out the possibility of CH₄ being the major product on TJU-26 (Fig. 5b). Overall, the reaction mechanism for the photocatalytic conversion of CO₂ to CH₃OH has been thoroughly investigated through a combination of *in situ* spectroscopic experiments and theoretical calculations.

Since the major oxidation half-reaction is experimentally determined to be EtOH oxidation, the competitive absorption behaviors of TJU-26 towards CH₃OH and EtOH are studied using vapor adsorption isotherms and contact angle

measurements. First, the hydrophobic nature of TJU-26 is confirmed by an average contact angle of 110.27°, suggesting that TJU-26 has a higher affinity towards EtOH rather than CH₃OH (Fig. 5c). The vapor adsorption isotherms of TJU-26 indicate the uptake amounts of 5.12 cm³ g⁻¹ for EtOH and 1.86 cm³ g⁻¹ for CH₃OH at 298 K under 1 bar (Fig. 5d). The substantially higher amount of EtOH adsorption suggests strong interactions between EtOH and TJU-26. Since the layered material has no apparent open pore window, the vapor adsorption probably occurs on the crystal surfaces of TJU-26. Given the substantially higher EtOH adsorption over CH₃OH adsorption, TJU-26 favors the desorption of CH₃OH as the product that agrees with the low desorption barrier of 0.17 eV based on DFT calculations (Fig. 5b).

Conclusions

In this study, we present the first example of a hybrid lead halide that can achieve photocatalytic CO₂-to-CH₃OH transformation. By incorporating an Fc-based ligand as a light-harvesting antenna into the ultrastable lead iodide framework, its visible-light absorption edge is extended to over 600 nm, followed by an efficient LMCT process that triggers carrier transport along the linear lead iodide chains. Compared to the control ionic Fc-based perovskite ((FMTMA)PbI₃), our lead iodide framework exhibits synergistic interactions between inorganic and organic photoactive components for enhanced carrier transport by multiple orders of magnitude. Notably, TJU-26 demonstrates high structural robustness in high-polar protic environments and achieves photocatalytic CO₂ reduction to high value-added CH₃OH under AM 1.5G irradiation, whereas most hybrid metal halides produce CO as the primary product. The AQE of TJU-26 for CH₃OH production reaches 0.41% at 400 nm, comparable to those of many benchmark photocatalysts (e.g., ¹⁰⁰CD/CN). Importantly, the oxidative half-reaction coupled with CO₂ photoreduction involves environmentally benign EtOH oxidation, resulting in the overall photocatalysis reaction in a sustainable manner. *In situ* DRIFT experiments and DFT calculations clearly indicate that the photocatalysis undergoes the formyl pathway to afford the key intermediate CH₃O*, which occurs on the dual Pb₂ active sites residing in [Pb₂I₂]²⁺ chains. Given the numerous examples of light-harvesting antenna-functionalized organocarboxylate linkers, we believe that this study opens up many possibilities for chemical functionalization of ultrastable lead halide frameworks for a variety of photoactive applications.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

J. Y., Y. H. and H. F. conceived the project. H. F. supervised the project. J. Y. and Y. H. performed the majority of experimental studies. C. S. assisted in the crystallographic analysis. Y. J.

assisted in the synthesis and photophysical studies. J. Y., Y. H. and H. F. wrote and revised the manuscript. All authors contributed to discussion and revisions.

Conflicts of interest

There are no conflicts to declare.

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