

Research Article

Photothermal-assisted full solar spectrum-driven CO₂ reduction by an azapentacene-based copper MOF

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Abstract

Photocatalytic CO₂ reduction is currently one of the most attractive researched topics, however, most photocatalysts to date can only utilize the energy from the ultraviolet and visible light spectrum, wasting the infrared light spectrum which occupies half of the solar spectrum energy. Herein, a novel full solar spectrum responsive metal-organic framework material based on azapentacene, named **CDN-1**, was designed and constructed. Its absorption profile covered the entire spectrum from 250 nm to 1500 nm. As a result, **CDN-1** demonstrated remarkable photothermal properties, with a rapid temperature increase up to 140 °C within 60 s upon 808 nm laser irradiation.

Electrochemical studies proved the potential of **CDN-1** for CO₂ photoreduction. With photothermal synergy, **CDN-1** displayed a CO₂ reduction rate of 656.8 μmol g⁻¹h⁻¹ for formic acid formation under white LED light, representing the highest performance among all copper-based metal-organic frameworks so far. Surprisingly, **CDN-1** also showed a reaction rate of 454.9 μmol g⁻¹h⁻¹ under natural sunlight. Ultrafast spectroscopic analysis of **CDN-1** indicated the presence of a photoinduced ligand-to-metal charge-transfer process, which was confirmed by X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and assisted by DFT calculations. This photoinduced electron transfer pathway was found to be responsible for **CDN-1**'s full solar spectrum absorption, excellent photothermal properties, and efficient photocatalytic CO₂ reduction performance.

Keywords: Full solar spectrum utilization, metal-organic frameworks, CO₂ photoreduction, photothermal, transient absorption

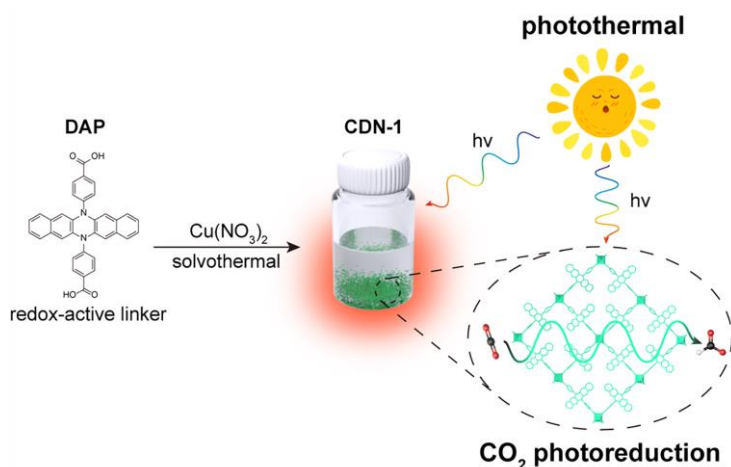
INTRODUCTION

The dependence of human civilization on fossil fuels has resulted in a marked rise in carbon dioxide (CO₂) emissions^[1,2], thereby intensifying the global warming crisis^[3,4]. Photocatalytic CO₂ reduction of artificial photosynthesis has been emerging as one of the most promising and sustainable approaches to simultaneously address the world's critical energy and environmental challenges^[5-9]. The development of suitable photocatalysts is thus of crucial importance to the realization of efficient photocatalytic CO₂ reduction reaction. In the last decades, a variety of materials ranging from inorganic semiconductors like TiO₂^[10], In₂O₃^[11], CdS^[12], ZnGa₂O₄^[13] and perovskite halide (CsPbBr₃)^[14] to organic semiconductors such as small molecular organic

dyes^[15], graphitic carbon nitride (g-C₃N₄)^[16] and covalent organic frameworks (COFs)^[17] have been widely investigated as photocatalysts. It is remarkable, however, to date many states of the art photocatalysts have their light absorption areas situated in the UV and visible light regions, while only a limited number of photocatalysts can utilize the near-infrared (NIR) light energy which accounts for nearly half of the solar energy^[18-23]. To fully harness the energy of the entire solar spectrum, the utilization of NIR light is indispensable. Therefore, the development of full solar spectrum responsive catalytic CO₂ reduction has attracted tremendous attention^[24]. But there still remains a great challenge for the rational design of such materials mainly due to the contradiction between light absorption (band gap energy) and the redox reaction dynamics (redox potentials) of narrow-band-gap photocatalysts. This means that as the band gap becomes smaller, it becomes more difficult for the reduction potential of the excited state electrons to match the redox potential required for the occurrence of photocatalytic reactions^[25]. A promising way to break this bottleneck is photothermal CO₂ catalysis which can not only convert low-energy NIR photons into heat to lower the system's energy barrier but also indirectly promote the photocatalytic CO₂ reduction process, thus circumventing the constraints of bandgap and redox potentials in narrow-band-gap photocatalysts^[26]. However, pure photothermal catalysis performance is not satisfactory because of the difficulties of designing stable narrow-band-gap materials as well as the limited photothermal conversion efficiency. Therefore, the development of a new class of materials capable of merging photocatalysis and photothermal catalysis to improve CO₂ reduction catalysis is of great significance.

Metal-organic frameworks (MOFs) are a class of organic-inorganic hybrid crystalline porous materials with unprecedented chemical and structural tunability and a broad range of applications^[27-37]. Compared to the conventional inorganic semiconductors and small-molecule and polymeric organic semiconductors, MOFs-based photo-catalytic materials for CO₂ photoreduction have several unique merits: (1) MOFs are composed of metal ions or clusters coordinated with organic linkers, in which both the inorganic and organic parts can act as light absorption centers; (2) it is common for MOFs to experience charge transfer transitions between metal nodes and organic linkers, which can further enhance light harvesting beyond intrinsic absorption; (3) the employment of suitable redox-active metals and organic linkers could tune the redox potential energy

level of MOFs to match with the CO₂ reduction potential; and (4) their porous structures could efficiently increase the amount of catalytically active sites and shorten the migration paths for photo-generated charge carriers and enhance the separation of electrons and holes. Due to the above advantages, MOFs-based materials have demonstrated their great potential as prospective photocatalysts for CO₂ reduction^[38-42]. Notably, some MOFs-based materials consisting of redox-active organic linkers or organic radicals have demonstrated highly efficient absorption of light in the visible and NIR region as well as very impressive near-infrared photothermal conversion ability^[43-45]. In this scenario, we speculate that a rational design of novel redox-active MOFs with full solar spectrum absorption would realize the integration of photocatalysis and photothermal catalysis to achieve full solar spectrum-driven highly efficient CO₂ reduction. Recently, our group has systematically investigated the redox properties of phenazine derivatives and their versatility in self-assembly, demonstrated that phenazine-based assemblies can form stable radical cations for catalyzing aza-Diels-Alder reactions and photoreductive dehalogenation^[46,47]. Besides, we have also disclosed that the increase in conjugation length of organic photocatalysts could significantly tune their photophysical and redox properties, and eventually affect the photocatalytic performance^[48]. On this basis, we deliberately design a new redox-active MOF consisting of Cu ions and a linker of azapentacene bearing two benzoic carboxylic acid sites. As the derivative of phenazine, azapentacene is expected to not only inherit the redox activity of phenazine moiety but also exhibit more excellent light-absorbing properties due to its extended conjugation length^[49]. Therefore, we anticipate that such azapentacene-based copper MOF could be a good candidate for full solar spectrum-driven CO₂ photoreduction [Scheme 1].



Scheme 1. Schematic diagram of the strategy adopted in this study.

In this study, a new full solar spectrum responsive copper metal-organic framework material based on azapentacene, named **CDN-1**, was elaborately designed and synthesized. The resultant **CDN-1** displayed unprecedented full solar spectrum responsive properties that its absorption spectrum covered the wavelength region from 250 nm to 1,500 nm. As a consequence, **CDN-1** exhibited excellent photothermal properties, e.g., the temperature of **CDN-1** could rapidly increase and reach a maximum of 140 °C within 60 s upon 808 nm laser irradiation. Electrochemical studies indicated that **CDN-1** possessed a more negative conducting band (CB) potential than the CO_2 reduction potential. Surprisingly, **CDN-1** serving as photocatalyst not only demonstrated a high CO_2 conversion rate of $656.8 \mu\text{mol g}^{-1}\text{h}^{-1}$ for formic acid formation under LED light irradiation but also exhibited a reaction conversion rate of $454.9 \mu\text{mol g}^{-1}\text{h}^{-1}$ under natural sunlight, which may represent one of the most efficient Cu-MOFs-based photocatalyst for CO_2 reduction to date. Ultrafast spectroscopic studies of **CDN-1** revealed the formation of a charge separation state and radical cation under illumination, suggesting the presence of a photoinduced ligand-to-metal charge-transfer (LMCT) process. This was further confirmed by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) studies, and assisted by DFT calculations, which collectively proved that the photoinduced electron transfer pathway within **CDN-1** accounted for its characteristic full solar spectrum absorption and its outstanding photothermal properties as well as photocatalytic CO_2 reduction performance.

EXPERIMENTAL

Materials and methods

All chemical reagents were used as received and were commercially available. The ^1H NMR and ^{13}C NMR spectra were obtained using the Bruker 500 MHz spectrometer; moreover, tetramethylsilane (TMS) or solvent peaks were used as an internal standard. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet.

Electrospray ionization (ESI) mass spectra were recorded with a Waters Synapt G2 mass spectrometer. The single crystals were measured on Rigaku XtaLAB PRO MM003-DS dual system with a Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV diffractor meter using Cu K α radiation at 35 kV and 25 mA in the 2θ angle range of $3\text{--}50^\circ$ using a step size of 0.02° and at a scanning speed of $2^\circ/\text{min}$. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer STA8000 instrument under a N_2 atmosphere in the temperature range of $30\text{--}800^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$. Gas sorption isotherms (N_2 and CO_2 , up to 1 bar) were measured on a Micromeritics ASAP 2020 surface area analyzer. Fluorescence spectra were recorded on HORIBA Duetta. Electrochemical and photoelectrochemical measurements were carried out on a CHI760E electrochemical workstation using a conventional three-electrode cell

Synthesis of 6,13-dihydrodiazapentacene (1)

2,3-dihydroxynaphthalene (930 mg, 5.8 mmol) and 2,3-diaminonaphthalene (930 mg, 5.8 mmol) were ground together with a mortar and pestle. The resulted solid was heated in an oil bath at 180°C under a nitrogen atmosphere for 1.5 h. The crude product was filtered and washed with MeOH several times. Pale green powder **1** was obtained in a yield of 80% (1.314 g).

Synthesis of 4,4'-(6,13-diazapentacene-6,13-diyl)dibenzoate (2)

A mixture of 6,13-dihydrodiazapentacene (**1**) (1.41 g, 5 mmol), methyl 4-bromobenzoate (4.30 g, 20 mmol), catalyst $\text{Pd}(\text{dba})_2$ (287.5 mg, 10 mol%), ligand RuPhos (205 mg, 10 mol%) and *t*-BuOK (2.24 g, 20 mmol) in anhydrous toluene (30 mL) was degassed by three freeze (77 K)-pump-thaw cycles. The mixture was stirred and heated at 110°C for 16 h. After cooling to room temperature, the mixture was

extracted with dichloromethane (DCM) (100 mL $\times$ 3). The combined organic phase was washed with brine (50 mL $\times$ 3). The organic phase was dried over anhydrous Na_2SO_4 and the organic solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel eluting with ethyl acetate: petroleum ether = 1: 20 to get pure product **2** (2.34 g) in 82% yield.

Synthesis of 4,4'-(6,13-diazapentacene-6,13-diyl)dibenzoic acid (DAP)

A suspension of compound **2** (2.75 g, 5 mmol) and NaOH (1.2 g, 30.0 mmol) in EtOH (20 mL) and THF (20 mL) was heated to reflux for overnight under argon. After cooling down to room temperature, the reaction mixture was poured into water. The concentrated HCl aq. solution (37%, 10 mL) was added into the mixture and product solid precipitated out. The solid was filtered and washed by water to give the crude compound. The crude product was purified by crystallization in EtOH solvent to give pure product **DAP** (2.61 g) in 93% yield.

Synthesis of CDN-1

$\text{Cu}(\text{NO}_3)_2$ (10 mg, 0.0429 mmol), 4,4'-(6,13-diazapentacene-6,13-diyl)dibenzoic acid (10 mg, 0.0192 mmol) were dissolved with 1.5 mL DMF and 0.2 mL H_2O in a Pyrex tube. The tube was degassed by three freeze-pump-thaw cycles, and then flame sealed under vacuum (the freezing step was carried out by cooling the reaction mixture with liquid nitrogen to 77 K). The reaction tube was put into an isothermal oven for 48 h and heated to 120 °C, yielding dark green cubic crystals (75% yield based on organic linkers).

Near-infrared photothermal conversion

About 100 mg of **CDN-1** was pressed into thin slices (1.8 cm in diameter) on a quartz slide and positioned 21.3 cm from an 808 nm laser (Hi-Tech Optoelectronics Co., Ltd., Beijing, China). Laser power density was varied from 0.1 to 0.7 W cm^{-2} . Infrared videos were recorded using a FLIR A6260 thermal camera, and images and temperature profiles were extracted with FLIR Tools software. Blank quartz glass showed negligible temperature change under 0.5 W cm^{-2} 808 nm laser irradiation for 60 s. Heating/cooling cycles were performed with a duration of 3 min per cycle.

Photocatalytic CO₂ reduction performance

The freshly prepared **CDN-1** was washed with DMF (20 mL $\times$ 3) to remove the adhesive ligand molecules on the crystals, followed by a solvent exchange process by soaking crystals in acetonitrile five times in three days to remove guest molecules such as DMF. The crystals were then evaporated under vacuum at 100 °C for 6 hours and stored at room temperature for further use. **CDN-1** (10 mg) was added into the CH₃CN/TEOA mixed solution (20 mL, v/v = 10/1) which has been pre-degassed with CO₂ to remove the dissolved O₂ for 1 hour. A white LED serves as the source of illumination, with an intensity of 448.5 mW/cm² and a wavelength range of 400 nm to 830 nm. The photocatalytic reactions are under a CO₂ atmosphere at ambient pressure, except the control experiment under N₂. The reaction was kept stirring constantly with a magnetic bar to ensure the photocatalyst particles in suspension. Controlled experiments include (1) dark reaction, (2) without **CDN-1**, (3) without TEOA, (4) replacement of **CDN-1** with **DAP**, (5) in N₂. The concentration of formate was detected by using a Thermo Scientific ICS-5000+ system and 30 mM KOH/ methanesulfonic acid solution was used as an eluent at a flow rate of 1.0 mL/min at 303 K.

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption (fs-TA) measurements were carried out on a Helios pump-probe system (Helios Fire, Ultrafast Systems) at room temperature. Pump pulses (400 nm, $\sim$ 10 μ J at the sample) were delivered by an OPerA SOLO optical parametric amplifier (Coherent Inc.) pumped by a Ti:sapphire regenerative amplifier (Astrella, 800 nm, 90 fs, 7 mJ, 1 kHz). White-light continuum probe pulses (420-750 nm) were generated by focusing a small portion of the 800 nm beam onto a sapphire plate. The instrument response function was $\sim$ 120 fs, determined via cross-correlation. Chirp-corrected transient absorption spectra were recorded with an optical fiber-coupled multichannel spectrometer and processed using Surface Explorer. Samples were contained in a 0.7 mL quartz cuvette under continuous magnetic stirring to maintain a fresh photoexcited volume.

RESULTS AND DISCUSSION

The linker 4,4'-(6,13-diazapentacene-6,13-diyl)dibenzoic acid (**DAP**) was designed and synthesized based on our previous work mainly involving a Buchwald-Hartwig coupling reaction and an ester hydrolysis reaction^[46,47] (details see the Supplementary Information (SI), section 1). Subsequently, the Cu-based metal-organic framework, denoted as **CDN-1**, was successfully prepared by a solvothermal reaction of Cu(NO₃)₂ and **DAP** in N,N-dimethylformamide (DMF) and water mixture at 120 °C for 48 hours. The structure of **CDN-1** was unambiguously confirmed by single crystal X-ray crystallography and the molecular formula was [Cu(DAP)(NMe₂)] [Figure 1]. X-ray crystallo-graphic analysis revealed that **CDN-1** crystallized in the monoclinic *C2/c* space group. Specifically, two Cu(II) cations and four carboxyl groups of **DAP** linker formed a paddle-wheel cluster capped with two dimethylamine cations to serve as secondary building units (SBUs), namely Cu₂(RCOO)₄(NMe₂)₂, which were linked together by azapentacene linker to generate a framework consisting of stacked square grids with an sql topology, where the distance between adjacent layers was around 2.5 Å [Figure 1A and Supplementary Figure 5A]. The direction of stacking did not align perpendicular to the layers but instead adopted a certain offset to facilitate π - π stacking [Figure 1B and 1C]. As a result, the azapentacene core exhibited a 160° bend shape in contrast to the flat molecular conformation of the free **DAP**, indicating the intrinsic conformation-adaptive of this phenazine derivative^[46,47] [Supplementary Figure 5]. The powder X-ray diffraction (PXRD) pattern of the as-prepared **CDN-1** exhibited a little peak broadening due to crystallite size and microstrain, but the pattern almost resembled the simulated one based on single-crystal X-ray diffraction data [Supplementary Figure 6B]. The scanning electron microscopy (SEM) observations demonstrate that **CDN-1** features a well-defined spherical morphology [Supplementary Figure 6c]. The thermogravimetric (TG) curve suggested that **CDN-1** was thermally stable up to 290 °C [Supplementary Figure 7]. The porosity of **CDN-1** was evaluated through N₂ adsorption analysis [Supplementary Figure 8], while their interaction with CO₂ was reflected by CO₂ adsorption experiments conducted at different temperatures [Supplementary Figure 9]. In particular, the nitrogen adsorption isotherm of the activated **CDN-1** at 77 K indicated a characteristic type II behavior with good reversibility, and its Brunauer–Emmett–Teller (BET) and total pore volume were then calculated to be 7.2217 m²/g and 0.0157 cm³/g, respectively [Supplementary Figure 8]. The CO₂ adsorption properties of **CDN-1** MOF at 1 atm revealed an uptake of 24.02 cm³/g and 8.91 cm³/g at 273 K and at room temperature (298 K), respectively

[Supplementary Figure 9]. Arguably, **CDN-1** exhibited significant affinity towards carbon dioxide even at room temperature given its characteristic microporosity, which would be vital to enhance its photocatalytic CO₂ reduction performance.

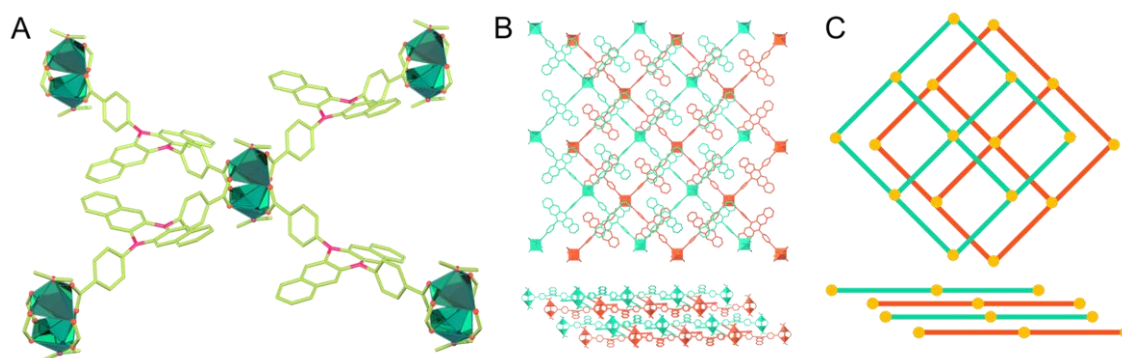


Figure 1. (A) Coordination environment of **CDN-1**, where light green, magenta, red, and dark green represent carbon, nitrogen, oxygen, and copper atoms, respectively. Hydrogen atoms and counter cations are omitted for clarity; (B) Top and side view of the stacking mode; (C) Topological structure of **CDN-1**.

The photophysical properties of **CDN-1** MOF was analyzed by UV-vis diffuse reflectance spectra (UV-vis DRS) [Figure 2A]. Surprisingly, the results of UV-vis DRS indicated that **CDN-1** featured an extremely broad range of light absorption covering the entire spectrum from the UV (250 nm) to the NIR (1500 nm), resulting in its dark green appearance. Consequently, the band gap energy of **CDN-1** can be estimated to be 1.26 eV from the Tauc plot derived from its UV-vis DRS [Figure 2B]. In contrast, the organic linker **DAP** was yellow color with the onset absorption edge of 420 nm and a ~ 2.92 eV band gap energy [Supplementary Figure 10]. We inferred that the distinct full solar spectrum absorption behavior of **CDN-1** could be attributed to the occurrence of ligand-to-metal charge-transfer (LMCT) between azapentacene core and Cu ions (*vide infra*)^[50]. Notably, the azapentacene core, as the derivative of phenazine, has the feature of outstanding redox activity and can be easily oxidized to generate stable radical cation species with strongly enhanced absorption [Supplementary Figure 11]^[49]. These properties allow for the stabilization of the holes generated after transferring an electron to the metal during the LMCT process, thus may serve as the driving force to enhance the LMCT. Considering its intriguing photophysical properties, the potential physiochemical processes and reactions that occur within **CDN-1** under light

irradiation were then surveyed by the photocurrent measurement [Figure 2C]. The results indicated the fast and uniform photocurrent responses within the **CDN-1** electrodes under light irradiation, indicating the efficient charge separation. Additionally, the photo responsive behavior of **CDN-1** was observed to be fully reversible, which was beneficial to its photothermal and photocatalytic activity. Mott-Schottky measurements were also conducted to evaluate the semi-conductive behavior of **CDN-1** MOF [Figure 2D]. The positive slope displayed in the plot at various frequencies was basically consistent with that of *n*-type semiconductors. The flat band position was determined to be approximately -0.40 V *vs.* NHE (i.e., -0.60 V *vs.* Ag/AgCl) from the intersection. Since in typical *n*-type semiconductors, the bottom of the conduction band (CB, analogous to the LUMO) could be regarded as equal to the flat band potential^[51,52], the conduction band (CB) of **CDN-1** can be estimated to be -0.40 V *vs.* NHE. The valence band (VB analogous to the HOMO) can then be calculated to be 0.86 V *vs.* NHE based on the conduction band and the optical band gap. Notably, proper redox potential of stimulated electrons is a vital requirement in the photoreduction of CO₂, and the more negative CB potential of **CDN-1** than the redox potential of CO₂ to formate (-0.28 V *vs.* NHE)^[53-56] implies that **CDN-1** as a full solar spectrum-driven catalyst is theoretically feasible for the photocatalytic CO₂ reduction reaction.

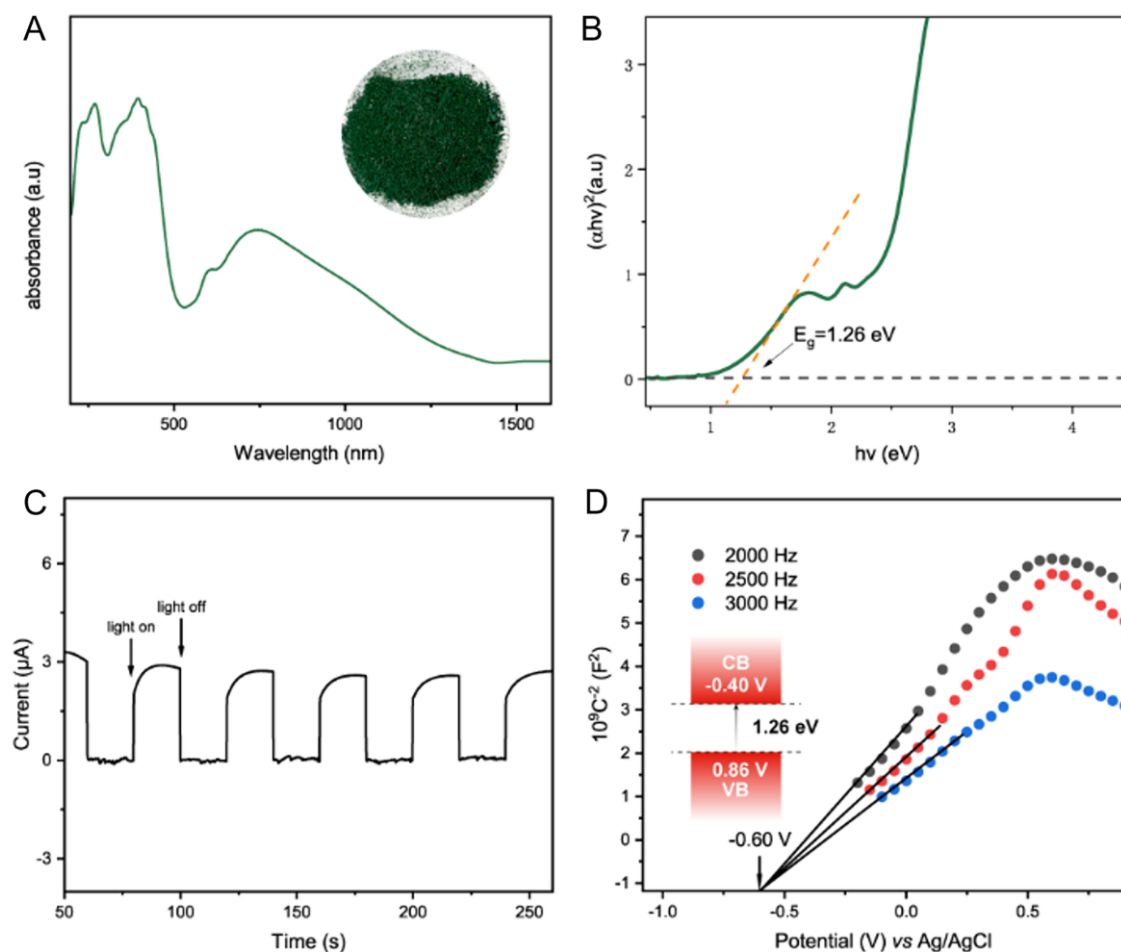


Figure 2. (A) UV-vis-NIR DRS spectra spectrum of **CDN-1**. The insets show the picture of **CDN-1** powder; (B) Tauc plot analysis showing the band gap of **CDN-1**; (C) Transient photocurrent responses of **CDN-1** electrode with light on/off cycles; (D) Mott-Schottky plot of **CDN-1** in 0.2 M sodium sulfate solution. The insets show the energy diagrams of the HOMO and LUMO levels of **CDN-1**.

Considering the pronounced full solar spectrum absorption capacity of **CDN-1**, its photothermal conversion efficiency was subsequently investigated by monitoring temperature changes using an IR camera (details see SI, section 3). As illustrated in Figure 3A, when a 1.8 cm diameter pallet of **CDN-1** powder was exposed to an 808 nm laser with an energy power of 0.7 W/cm², the temperature increased rapidly from 22.8 °C to approximately 140 °C within 40 s and reached a maximum of 142.2 °C through a quasi-steady state period of 200 s (see SI video). Remarkably, the temperature decreased rapidly to 30 °C within 60 s after laser removal, indicating a fast photothermal conversion response of **CDN-1**. We determined a photothermal conversion efficiency of $46.9 \pm 1.0\%$ at 0.7 W/cm² from the heating-cooling curve data

[Supplementary Information Section 3, Supplementary Figure 12], which was relatively high compared with those of other reported MOFs [Supplementary Table 2]. By varying the energy power to 0.1, 0.3, and 0.5 W/cm², the maximum temperatures of **CDN-1** were altered to 41.0, 87.3, and 112.6 °C in 240 s, respectively [Figure 3B]. Moreover, a cyclic test was performed on **CDN-1**, with six repeated illumination cycles across all four power densities, and no significant degradation in its performance was observed [Figure 3C]. The PXRD pattern analysis conducted after the cycling experiments also confirmed its good photostability [Supplementary Figure 13]. These results verify that **CDN-1** possesses remarkable photothermal conversion properties, which are comparable to those of the most state-of-the-art photothermally active MOF under light irradiation [Figure 3D]^[43-45,57-62]. We propose that the superior photothermal performance of **CDN-1** is attributed to its efficient charge separation process followed by a fast non-radiative relaxation, which suppresses the radiative recombination of the excited carriers upon electron transition from the valence band to the conduction band upon photon absorption. This significantly reduces the release of energy in the form of photons and thus enhances the photothermal conversion efficiency of **CDN-1**. It is worth mentioning that some recent studies have demonstrated that photothermal synergy can spark the reduction of CO₂ over semiconductor photocatalysts, e.g., photothermal effect can increase the temperature to reduce the apparent activation energy based on the Arrhenius equation, boost the transfer rate of photogenerated carriers, and accelerate the rate of mass transfer and adsorption of reactants^[63-66]. Therefore, we believe that the excellent photothermal properties of **CDN-1** MOF lay a solid foundation for its full-spectrum solar light-driven CO₂ catalysis.

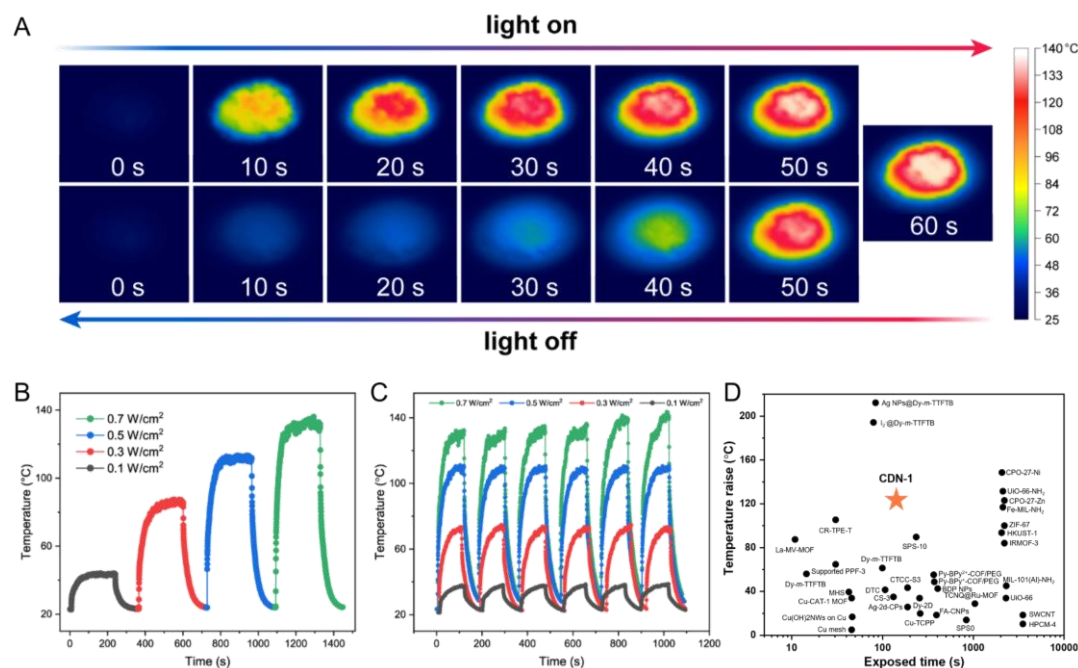


Figure 3. (A) The IR thermal images of **CDN-1** MOF powder (diameter = 1.8 cm) under 0.7 W/cm² which was then turned off; (B) Photothermal conversion curves of **CDN-1** at different NIR laser intensities; (C) Anti-photobleaching property of **CDN-1** radical MOF powder during six heating-cooling cycles; (D) The temperature change of various solid-state photothermal materials reported in the references.

The CO₂ photoreduction measurements were performed under visible-light irradiation (12 W white light LED as the light source) and a pure CO₂ (1.0 atm, 293 K) atmosphere in acetonitrile with triethanolamine (TEOA) as electron donor and hydrogen donor source (details see SI, section 4). The liquid products after the reaction were detected by ion chromatography and a main product of HCOO⁻ was conformed [Supplementary Figure 14]. We also tried to detect the gaseous products through gas chromatography. No gaseous product such as CO, CH₄, or H₂ can be detected [Supplementary Figure 15], suggesting that **CDN-1** was highly selective toward CO₂ reduction to formate. The product of HCOO⁻ was quantified through ion chromatography during the catalytic process and demonstrated a time-dependent HCOO⁻ amount increase under continuous visible light illumination [Figure 4A]. The average generation rate of HCOO⁻ was determined to be ~ 656.8 μmol g⁻¹h⁻¹, which may represent the best performance of visible-light-driven CO₂ photoreduction to formate catalyzed by Cu-based MOFs as far as we know [Supplementary Table 5]. The corresponding apparent quantum yield (AQY) and turnover frequency (TOF) were

calculated to be 0.174% and 0.438 h^{-1} , respectively. It should be noted that the temperature of the reaction mixture, especially near the photocatalyst **CDN-1**, obviously increased during the reaction process [Figure 4B], indicating that photothermal effects were involved and played a role in the catalytic process. To further validate the excellent full-spectrum photothermal performance of **CDN-1**, control experiments were conducted under monochromatic light irradiation at 380 nm, 600 nm, and 1064 nm. As shown in Supplementary Figures 16 and 17, both 380 nm and 600 nm irradiation effectively activated the catalytic activity of the MOFs, leading to HCOO^- generation rates of 11.53 and $128.7\text{ }\mu\text{mol g}^{-1}\text{h}^{-1}$, respectively. In contrast, a relatively lower rate of HCOO^- formation ($1.42\text{ }\mu\text{mol g}^{-1}\text{h}^{-1}$) was observed under 1,064 nm irradiation [Supplementary Figure 18]. These results clearly demonstrate that **CDN-1** was capable of harvesting light across the entire spectral range, although its catalytic efficiency decreases slightly in the near-infrared region. Furthermore, to quantitatively assess the specific contribution of the photothermal effect to CO_2 reduction, we performed control experiments of pure photocatalysis under constant temperature conditions. In these experiments, all other parameters were kept identical while the reaction temperature was maintained at 288 K. As shown in Supplementary Figure 19, under these isothermal conditions, the average generation rate of HCOO^- decreased to approximately $14.43\text{ }\mu\text{mol g}^{-1}\text{h}^{-1}$, indicating that the heat produced by the MOF upon light irradiation indeed plays a synergistic role in promoting the CO_2 conversion process. Encouraged by its fantastic photothermal and photocatalytic activity, natural-sunlight-driven photoreduction of CO_2 by **CDN-1** was then demonstrated [Supplementary Figure 20]. To our delight, the photocatalytic CO_2 reduction to HCOO^- driven by solar light can be achieved with comparable conversion and yield performance ($454.9\text{ }\mu\text{mol g}^{-1}\text{h}^{-1}$) to that under an artificial light source in similar conditions [Supplementary Figure 21]. This outstanding outcome strongly supports the conclusion that **CDN-1** as a full-spectrum responsive photocatalytic material is highly effective in capturing and utilizing a significant amount of solar energy. Moreover, the heterogeneous **CDN-1** can be readily separated and recovered from the reaction by centrifugation. Recycling experiments were performed to evaluate the stability of **CDN-1**, which demonstrated that no noticeable change in the yield rate of HCOO^- occurred during the four reaction runs [Figure 4C]. The powder X-ray diffraction (PXRD) profile further revealed that the structure of **CDN-1** remained almost unchanged after the reaction [Supplementary Figure 22]. Likewise, ICP-OES analysis

demonstrated that the concentration of copper ions leached into the solution was negligibly low (≈ 102 ppm), thereby unambiguously confirming that the catalytic activity originates intrinsically from the heterogeneous catalyst **CDN-1** rather than from any dissolved copper species. The photocatalytic CO_2 reduction was further confirmed by a series of controlled experiments including (1) dark reaction, (2) without **CDN-1**, (3) without TEOA, (4) replacement of **CDN-1** with **DAP**, (5) in N_2 , and (6) isotopic label using $^{13}\text{CO}_2$ [Supplementary Figure 23]. These results clearly displayed that, no formate was generated when the catalytic reactions were performed in the dark at 100°C or in the absence of **CDN-1** or TEOA [Supplementary Figure 23]. When the catalytic reaction was conducted in an N_2 atmosphere instead of CO_2 , no HCOO^- was formed either [Supplementary Figure 23]. Further, the photocatalytic experiment was also performed using $^{13}\text{CO}_2$ to confirm the origin of HCOO^- . The ^{13}C NMR spectrum of the in-situ reaction mixture displayed a peak at 164.8 ppm which well corresponds to the product of $\text{H}^{13}\text{COO}^-$ [Figure 4D]. Therefore, these results conclusively prove that CO_2 is the main carbon source for production of HCOO^- , eliminating the possibility of contamination from other carbon-containing species. Interestingly, a small amount of HCOO^- (~ 6.3 μmol) was also produced under similar conditions when the organic linker was employed as the photocatalyst [Figure 4A], indicating the intrinsic photocatalytic activities of azapentacene moiety. As a result, when the organic linker **DAP** was combined with Cu moiety, the resultant **CDN-1** significantly boosted the photocatalytic CO_2 reduction reaction.

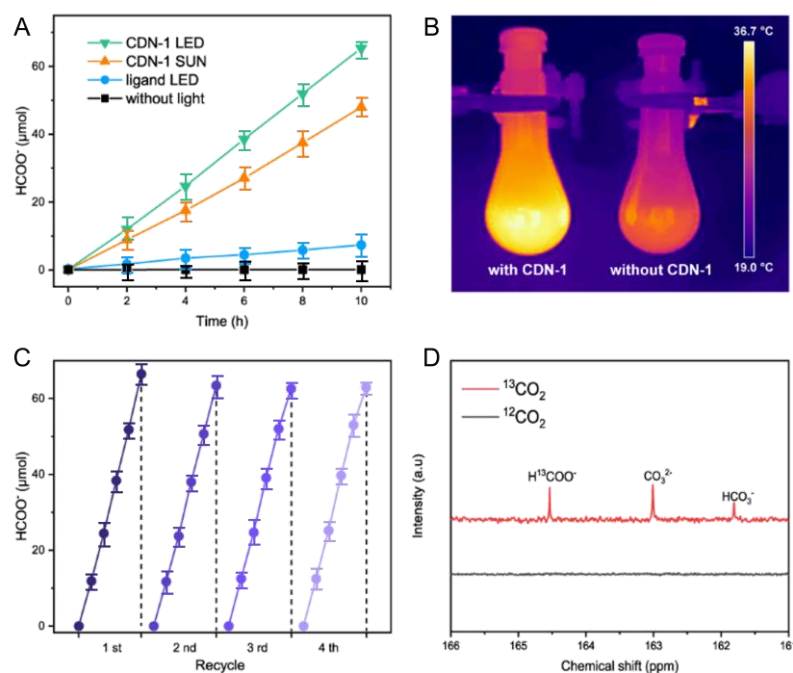


Figure 4. (A) Changes in HCOO^- concentration as a function of irradiation time under different conditions; (B) The IR thermal images of photocatalysis system compared with a control condition; (C) The recycle experiments of used **CDN-1**, in which the catalyst was recovered by centrifugation and redispersed in a fresh acetonitrile solution for a 10 hours reaction; (D) ^{13}C NMR spectra of liquid product from photoreduction of $^{13}\text{CO}_2$ (red) and CO_2 (black) by **CDN-1** for 10 h under NIR light.

To gain insight into the superior full-spectrum-light-driven photocatalytic activity of **CDN-1**, we conducted a thorough analysis of the photoexcited dynamics involved in the neutral linker **DAP**, radical cation species **DAP^{•+}** and **CDN-1** MOF by using femtosecond transient absorption spectroscopy (fs-TA), a technique for real-time monitoring of charge carrier dynamics with femtosecond time resolution^[67-69] (details see SI, section 5). The pump wavelength was selected to be 400 nm, which can effectively excite all above three objects. The TA spectra shown here were plotted as differential transmission of probe in the range of 450–750 nm. For **DAP**, two excited-state absorption (ESA) peaks at around 453 and 557 nm [Figure 5A and 5B, Supplementary Figure 25] appeared right after excitation, while the ground state bleach (GSB) was not observed because its absorption onset in the steady-state absorption spectrum actually started at 440 nm. There were barely any spectra shift rather than amplitude decay seen in **DAP**, and the life-times were determined to be 13.5 ± 0.2 , 123 ± 3 , 685 ± 3 and a long-lived offset, respectively [Supplementary Figures 28-30]. The decay associated different spectra (DADS) of **DAP** were also extracted from global fitting and displayed in Figure 5C. It is clear that DADS-1 (black) is almost a mirror image of DADS-2 (red) and DADS-3 (blue), suggesting that DADS-1 is a precursor of DADS-2 and DADS-3. Since the 685 ps lifetime of DADS-3 matches well with the 0.7 ns lifetime found in the time-resolved PL measurement [Supplementary Figure 38], it can be assigned to this major emissive decay channel in **DAP**, which could arise from charge recombination in **DAP**. Because of the highly spectral similarity between DADS-2 and DADS-3, DADS-2 should also arise from a decay channel due to charge recombination of **DAP**, yet it has a shorter lifetime. At last, DADS-4 should response to the longer emission lifetimes seen in the time-resolved PL measurement.

For comparison, the radical cation analogue **DAP^{•+}** was also examined under similar conditions [Figure 5D and 5E, Supplementary Figures 26, 31-33], but with

dichloromethane as the solvent instead, as DMF could reduce the radical cation to its neutral form. Right after excitation, the radical cation **DAP^{•+}** displayed very similar TA spectra compared with **DAP**. Yet, there is an extra small ESA peak centered around 620 nm as well as a bleach band at 587 nm. While this bleach band could arise due to the enhanced absorption of **DAP^{•+}** in this region [Supplementary Figure 26], the newly appeared TA signals resemble typical TA spectra feature reported in systems with strong Stark effect^[70], suggesting effective charge transfer in **DAP^{•+}**. In this case, DADS-1 and DADS-2 should also be assigned to the charge transfer process in **DAP^{•+}** due to the clear spectra features from Stark effect while DADS-3 should arise from charge recombination [Figure 5F].

Interestingly, the fs-TA spectra of **CDN-1** MOF not only displayed ESA band at 453 and 557 nm that closely resembled those of the neutral linker **DAP**, but also exhibited much stronger signals at 580 and 620 nm, respectively [Figure 5G and H, Supplementary Figure 27]. These results indicate that charge transfer is enhanced due to a ligand-to-metal charge transfer (LMCT) process after **DAP** is assembled into the MOF. Specifically, due to the strong electron-donating nature of azapentacene core, the electron of the **DAP** linkers could be excited upon light irradiation and transferred to the surrounding copper ions, leaving behind a hole that forms an azapentacene cationic radical. The bleach peak at 555 nm and ESA peak at 620 nm seen in DADS-1 of **CDN-1** should arise due to much stronger Stark effect in **CDN-1**, which is direct evidence for effective LMCT [Figure 5I]. While the intrinsic charge recombination channel with hundreds of ps lifetimes (DADS-2 and DADS-3) still exist in **CDN-1**, the amplitude of the long-lived component (DADS-4) is much larger in **CDN-1** [Figure 5I]. The negative TA signals of DADS-4 should arise from the long-lived electrons in the MOF skeleton which block the ground state absorption. The lifetime of DADS-4, probably a few tens to hundreds of nanoseconds or even at microsecond scale, exceeded the detection window of our TA spectrometer. The presence of such long-lived species suggests the existence of electrons are trapped in the bandgap of **CDN-1**, as the characteristic lifetimes of such states (which characterize the electron-detrapping rates) typically fall within the nanosecond time domain based on the related report^[71]. The steady-state photoluminescence (PL) spectra of **CDN-1** MOF and **DAP** linker were examined to study their luminescent properties, which can provide some insights into

radiative carrier recombination. The absorption intensity of **CDN-1** was found to exhibit a drastic decrease when compared to those of the pristine linker [Supplementary Figure 37]. This pronounced PL emission quenching indicated effective charge transfer in **CDN-1** MOF. Additionally, the fluorescence lifetime of **CDN-1** was shorter than that of the linker [Supplementary Figures 38 and 39]. The reduced PL decay lifetime and intensity observed in **CDN-1** could also be attributed to the non-radiative electron transfer occurring between the linker and Cu cluster, namely, LMCT. Therefore, the fs-TA and steady-state PL results collectively suggested that **CDN-1** MOF displayed dramatically different photoexcited dynamics and carrier recombination processes, largely because the existence of ligand-to-metal charge transfer in the MOF. It is because of such LMCT that **CDN-1** MOF possesses distinct absorption features in both near-infrared and visible region, and consequently resulting in its excellent photothermal and photocatalytic activity.

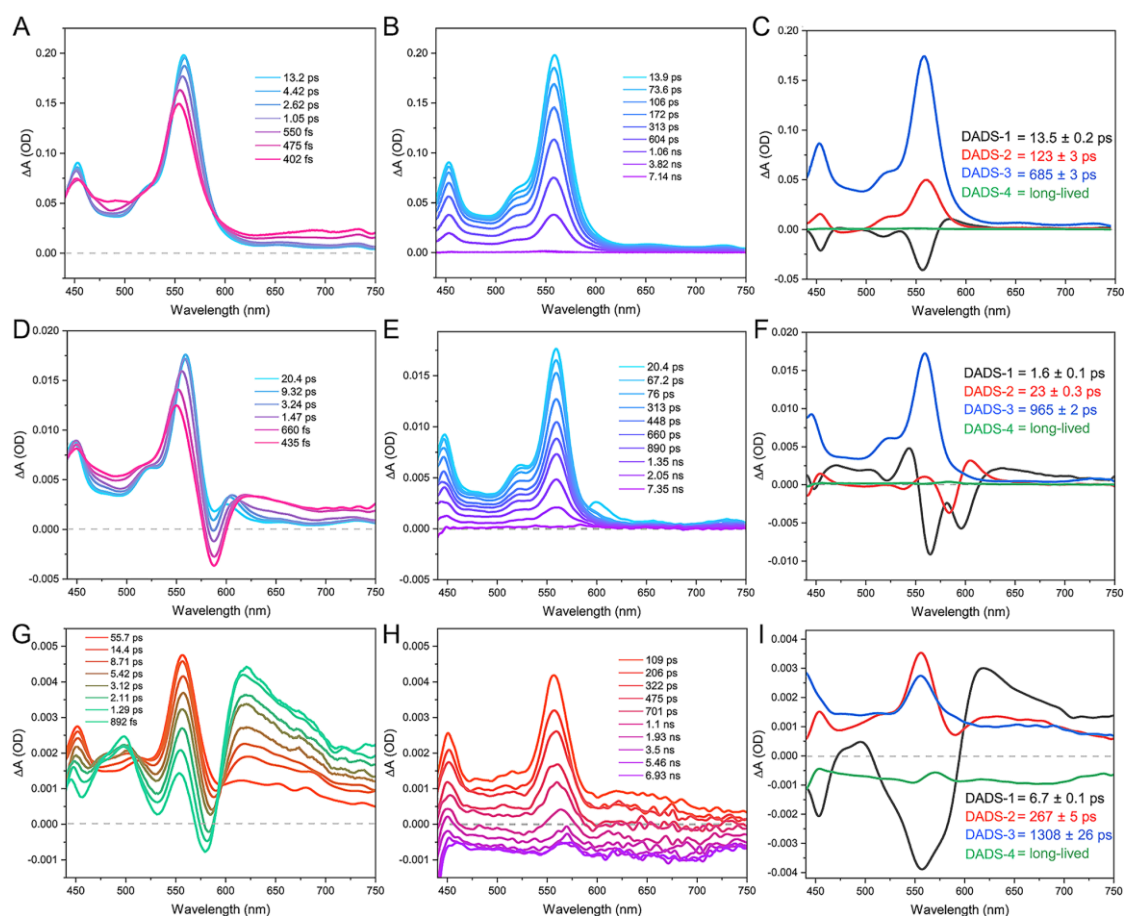


Figure 5. (A) fs-TA spectra of **DAP** linker from 475 fs to 13.2 ps under 400 nm excitation; (B) fs-TA spectra of **DAP** linker excited from 13.2 ps to 7.14 ns; (C) The DADS of **DAP** linker; (D) fs-TA spectra of **DAP** linker radical cation from 435 fs to

20.4 ps under 400 nm excitation; (E) fs-TA spectra of **DAP** linker from 20.4 ps to 7.35 ns; (F) The DADS of **DAP** linker radical cation; (G) fs-TA spectra of **CDN-1** from 892 fs to 55.7 ps under 400 nm excitation; (H) fs-TA spectra of **CDN-1** 55.7 ps to 6.93 ns; (I) The DADS of **CDN-1**.

The LMCT in **CDN-1** MOF was further demonstrated by electron paramagnetic resonance (EPR) spectroscopy and X-ray photoelectron spectroscopy (XPS). **DAP** linker was found to be EPR silent while **CDN-1** MOF exhibited a characteristic EPR spectrum [Figure 6A]. Specifically, **CDN-1** featured a broad EPR signal ($g \approx 2.05$) corresponding to Cu(II) species and a single line from organic free radical ($g = 2.002 \sim 2.003$) which is likely to stem from the electron transfer species of azapentacene moiety. Thus, the preliminary EPR data suggested the presence of LMCT process in **CDN-1** MOF, that accounted for the observed organic radical signal. Furthermore, XPS analyses were performed on **CDN-1** before and after the catalytic reaction to investigate the valence state evolution of the Cu centers. As shown in Supplementary Figure 24 and Supplementary Table 4, Cu(II) was predominant in **CDN-1** prior to the reaction. However, after exposure to white light and completion of the catalytic process, all copper ions were converted to Cu(I) species [Figure 6B]. This observation provides strong evidence that a ligand-to-metal charge-transfer (LMCT) process occurs within **CDN-1** during the catalytic cycle. This result further indicated that the photoinduced electrons from the organic linker were transferred to the metal SBUs, resulting in the formation of Cu(I) species. In addition, the time-dependent DFT calculations of the model structure of **CDN-1** MOF disclosed that the long-wavelength absorption bands of **CDN-1** were mainly ascribed to excitation from ground state S_0 to singlet excitation state S_7 and S_0 to S_{13} [Supplementary Figures 40 and 41]. Further natural transition orbital analysis shows that both $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_{13}$ excitations involve the transition from π orbitals of ligand **DAP** to d orbitals of Cu, especially for the excitation of $S_0 \rightarrow S_7$ [Supplementary Figures 40 and 41]. Thus, it indicates an obvious ligand to metal charge transfer characters between **DAP** and Cu ions. Therefore, based on the experimental and calculation results, a plausible mechanism for CO₂ photoreduction over **CDN-1** is proposed [Figure 6C]: when the reaction system is illuminated, the DAP linker moieties are excited and then transfer electrons to the Cu-oxo clusters to reduce the metal centers from Cu(II) to Cu(I), namely photoinduced

LMCT; the resulting Cu(I) species serve as the active sites for reducing CO_2 to HCOO^- and are subsequently oxidized back to Cu(II); TEOA acts as an electron donor and proton source, consuming the photoinduced holes and facilitating selective $^*\text{COO}^-$ protonation for HCOO^- .

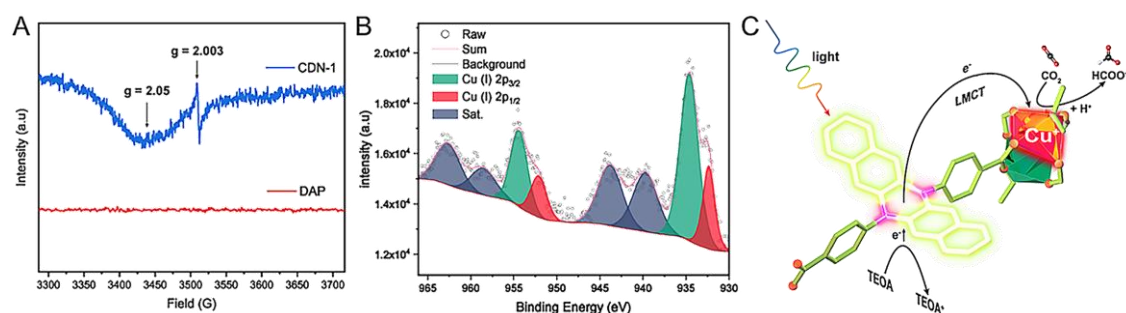


Figure 6. (A) EPR spectra of **CDN-1** and the **DAP** ligand; (B) XPS spectra of **CDN-1** after white light illumination; (C) Schematic representation of the mechanism of **CDN-1** photocatalytic reduction of CO_2 driven by full solar spectrum.

CONCLUSIONS

In summary, we designed and constructed a new full solar spectrum responsive metal-organic framework material **CDN-1**. By judicious ligand selection, we successfully integrated photothermal effect and photocatalysis into this MOF. **CDN-1** demonstrated excellent broad absorption covering from UV to infrared regions and impressive photothermal conversion performance. With the aid of photothermal synergy, **CDN-1** can not only convert CO_2 to formate at a rate of $656.8 \mu\text{mol g}^{-1}\text{h}^{-1}$ under white LED light but also perform photocatalysis successfully under sunlight irradiation. The results of transient absorption spectroscopy provided strong evidence for ligand-to-metal charge transfer within **CDN-1**. The conclusion was further confirmed by electron paramagnetic resonance and X-ray photoelectron spectroscopy experiments. We hope that this work will shed some light on the rational design of novel efficient narrow-band-gap photocatalyst with full-spectrum absorption in the future.

DECLARATIONS

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Authors' contributions

Made substantial contributions to conception and design of the study and performed data analysis and interpretation: Shi, X.; Yang, H. B.; Li, M.; Huang, B.

Performed fs-TA spectra data acquisition and analysis: Jia, M.; Wang, X.; Chen, J.

DFT calculations: Luo, Z.; Hu, L.

Single crystal analyses: Niu Y. F.; Zhao X. L.

Availability of data and materials

Data supporting the findings of this study are available within this Article and its Supplementary Materials. Further data is available from the corresponding authors upon reasonable request.

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Conflicts of interest

Yang, H. B. is Associate Editor of the journal *Chemical Synthesis*. Yang, H. B. was not involved in any steps of editorial processing, notably including reviewers' selection, manuscript handling and decision making. The other authors declare that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Graphical Abstract

