

Interfacial electronic coupling in copper 4-cyanophenylacetylide/copper phenylacetylide regulates molecular oxygen activation through coupled electron and energy transfer

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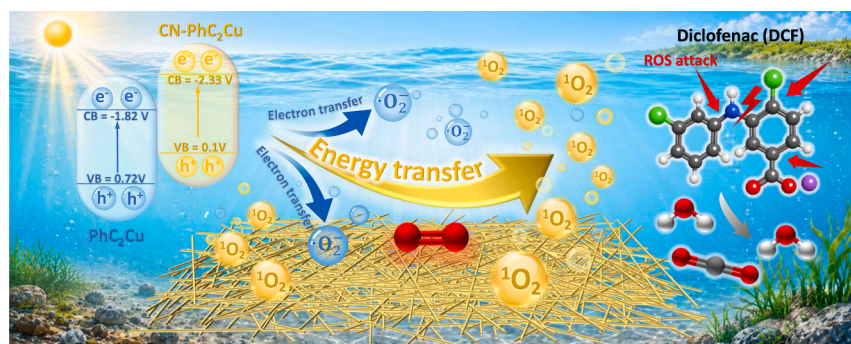
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GRAPHICAL ABSTRACT



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ABSTRACT

Interfacial regulation of molecular oxygen activation is critical for controlling reactive oxygen species generation in photocatalytic systems. Here, a copper 4-cyanophenylacetylide/copper phenylacetylide heterointerface (CN-PhC₂Cu/PhC₂Cu) was constructed through a one-step in situ strategy to regulate interfacial charge transfer and excited-state processes. Cyano functionalization created an electronic difference between the two copper acetylide components, while their related C≡C—Cu coordination frameworks favored intimate interfacial coupling. The optimized 75CNPC removed 95.2 ± 3.9% of diclofenac within 60 min under 455 nm visible-light irradiation and retained appreciable activity in the presence of common water constituents and in different aqueous matrices. Optical, electrochemical, and theoretical analyses indicate that interfacial coupling modulates the local electronic structure, facilitates charge separation, and strengthens O₂ adsorption. Reactive oxygen species (ROS) measurements further reveal a redistribution of O₂ activation channels: electron transfer contributes to ·O₂⁻

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formation, whereas interface-regulated excited-state processes favor triplet-mediated energy transfer and enhanced $^1\text{O}_2$ generation. Liquid chromatography-mass spectrometry (LC-MS) analysis and toxicity evaluation suggest that DCF undergoes initial activation, structural fragmentation, and progressive oxidation, with several identified transformation products exhibiting reduced predicted toxicity relative to the parent compound. These results demonstrate how the CN-PhC₂Cu/PhC₂Cu coordinates charge transfer, excited-state evolution, and molecular oxygen activation in organometallic photocatalysts.

1. Introduction

Molecular oxygen activation in heterogeneous photocatalysis is governed by a series of coupled processes occurring at the catalyst-water-oxygen interface, including O₂ adsorption, interfacial charge transfer, excited-state evolution, and reactive oxygen species (ROS) generation [1]. Heterojunction engineering has been widely employed to promote photogenerated carrier separation; however, improvements in photocatalytic activity are still commonly interpreted mainly in terms of enhanced charge-transfer efficiency [2,3]. Comparatively less attention has been paid to how interfacial electronic coupling regulates the balance between electron-transfer and energy-transfer channels during O₂ activation. This issue is important because different activation channels generate ROS with distinct reactivities and selectivities [4,5]. Therefore, constructing structurally compatible interfaces with sufficient electronic asymmetry provides a rational strategy for controlling interfacial O₂ activation and ROS generation [6].

Pharmaceuticals and personal care products (PPCPs) are continuously discharged into aquatic environments through domestic wastewater, medical effluents, and wastewater-treatment-plant outflows. Owing to their structural stability and biological activity, these contaminants are often incompletely removed by conventional treatment processes and may pose long-term ecological risks [7,8]. Visible-light-driven photocatalysis is considered a promising treatment technology because it can generate ROS in situ and promote the oxidative transformation of pharmaceutical contaminants under mild conditions [9]. Nevertheless, its efficiency is frequently limited by rapid recombination of photogenerated carriers, inefficient interfacial charge utilization, and insufficient O₂ adsorption and activation [10]. Since the type and distribution of ROS directly influence degradation kinetics and molecular transformation routes, regulating O₂ activation through interfacial electronic-structure engineering is essential for developing efficient photocatalytic systems [11,12]. Different ROS play distinct roles in photocatalytic oxidation. Hydroxyl radicals ($\cdot\text{OH}$) possess strong oxidation ability but low selectivity and are readily scavenged by inorganic anions and natural organic matter [13]. Superoxide radicals ($\cdot\text{O}_2^-$), generated through the one-electron reduction of O₂, are important intermediates in molecular oxygen activation and can participate in the initial transformation of organic molecules. By contrast, singlet oxygen ($^1\text{O}_2$) is a representative non-radical ROS that preferentially reacts with electron-rich aromatic structures, unsaturated bonds, and heteroatom-containing functional groups, while showing greater tolerance toward some background water constituents [14]. The complementary participation of $\cdot\text{O}_2^-$ in initial activation and $^1\text{O}_2$ in selective oxidation can therefore facilitate the progressive transformation of structurally stable contaminants. In addition to electron-transfer reactions, $^1\text{O}_2$ can be generated through an energy-transfer pathway, in which photoexcited singlet states undergo intersystem crossing to triplet states, followed by energy transfer to ground-state triplet oxygen ($^3\text{O}_2$) [4]. Coordinating interfacial charge transfer with triplet-state energy transfer is thus a promising approach for regulating O₂ activation pathways and ROS selectivity.

Copper phenylacetylide (PhC₂Cu) is an organometallic semiconductor composed of an extended $\text{C}\equiv\text{C}-\text{Cu}$ coordination framework, an ordered π -conjugated structure, and metal-alkynyl electron-transport channels [15]. Its visible-light response, tunable organic ligands, and adjustable coordination environment provide considerable flexibility for

regulating local electronic states, carrier migration, and molecular oxygen activation. However, pristine PhC₂Cu still suffers from rapid electron-hole recombination, limited charge utilization, and insufficient O₂ adsorption and activation, which restrict its photocatalytic performance, particularly in complex aqueous matrices [10]. To address these limitations, previous studies have developed copper acetylide-based photocatalysts through ligand functionalization, elemental regulation, and heterojunction construction. For example, cyano functionalization has been used to regulate the electronic structure of PhC₂Cu, thereby improving its photocatalytic performance toward DCF [16]. However, this strategy is limited to a single copper acetylide component and does not involve interfacial electronic coupling. Moreover, while PhC₂Cu-based Z-scheme heterojunctions (e.g., UiO-66-NH₂/PhC₂Cu [17] and Bi₂WO₆/PhC₂Cu [18]) improve charge separation, they mainly focus on charge-transfer-driven ROS production and overlook potential energy-transfer pathways. Based on these considerations, coupling Copper 4-cyanophenylacetylide (CN-PhC₂Cu) with PhC₂Cu combines their closely related $\text{C}\equiv\text{C}-\text{Cu}$ coordination frameworks with cyano-induced electronic asymmetry, thereby creating a structurally compatible and electronically asymmetric heterointerface [19,20]. This interfacial design provides an opportunity to coordinate interfacial charge transfer and triplet-state energy transfer during O₂ activation.

In this work, a CN-PhC₂Cu/PhC₂Cu heterointerface was constructed through a one-step in situ strategy, and diclofenac (DCF) was selected as a representative pharmaceutical contaminant to evaluate photocatalytic performance and reaction mechanisms. The study focuses on how cyano-induced electronic asymmetry and interfacial coupling regulate local electronic structure, carrier separation, excited-state behavior, O₂ adsorption and activation, and the generation of $\cdot\text{O}_2^-$ and $^1\text{O}_2$. Structural and photoelectrochemical characterization, ROS identification, excited-state analysis, theoretical calculations, aqueous-matrix experiments, liquid chromatography-mass spectrometry (LC-MS) analysis, and toxicity evaluation were integrated to establish the relationship between interfacial electronic regulation and molecular oxygen activation. This work elucidates how the CN-PhC₂Cu/PhC₂Cu coordinates electron-transfer and energy transfer pathways and provides a mechanistic basis for regulating O₂ activation and ROS generation in organometallic photocatalytic systems.

2. Materials and methods

2.1. Reagents and materials

Sodium diclofenac (DCF, >99.0%), copper(II) chloride dihydrate (CuCl₂·2H₂O, analytical grade), triethylamine (Et₃N, analytical grade, 99.0%), phenylacetylene (PhA, 97.0%), 4-ethynylbenzonitrile (98.0%), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, GC grade, >98.0%), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL, GC grade, >98.0%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%), tert-butanol (TBA, analytical grade, >99.0%), furfuryl alcohol (FFA, analytical grade, 98%), 2,2,6,6-tetramethylpiperidine (TEMP, >98.0%), 1,3-diphenylisobenzofuran (DPBF, >98.0%), terephthalic acid (TPA, analytical grade, >99.0%), Sorbic acid (HDA, >99.0%), deuterium oxide (D₂O, 99.9 atom% D), and sodium hydroxide (NaOH, analytical grade, 98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Potassium bromate (KBrO₃, analytical grade, 99.8%) and nitro blue tetrazolium chloride (NBT,

98.0%), barium sulfate (BaSO_4 , analytical grade, $\geq 99.0\%$), and potassium chloride (KCl , analytical grade, $\geq 99.5\%$) were obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) was supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China). Ciprofloxacin (CIP), sulfadiazine (SDZ), ofloxacin (OFX), enrofloxacin (ENR), sulfafurazole (SIZ), and fleroxacin (FLX) were analytical-grade reagents purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Methanol (MeOH , analytical grade, $\geq 99.7\%$), ethanol (EtOH , analytical grade, $\geq 99.7\%$), hydrochloric acid (HCl , analytical grade, $\geq 99.7\%$), and sodium sulfate (Na_2SO_4 , analytical grade, $\geq 99.0\%$), Ferric chloride (FeCl_3 , analytical grade, $\geq 99.7\%$), ammonium chloride (NH_4Cl , analytical grade, $\geq 99.7\%$), sodium carbonate (Na_2CO_3 , analytical grade, $\geq 99.7\%$), sodium bicarbonate (NaHCO_3 , analytical grade, $\geq 99.0\%$), sodium nitrate (NaNO_3 , analytical grade, $\geq 99.7\%$), calcium chloride (CaCl_2 , analytical grade, $\geq 99.0\%$), magnesium chloride (MgCl_2 , analytical grade, $\geq 99.7\%$), and humic acid (HA, analytical grade, $\geq 99.0\%$) were purchased from Tianjin Damao Chemical Reagent Co., Ltd. (Tianjin, China). HPLC-grade methanol and formic acid (HPLC grade, $\geq 98.0\%$) were purchased from Shanghai ANPEL Laboratory Technologies Inc. (Shanghai, China). Nafion solution was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water ($18.25 \text{ M}\Omega\cdot\text{cm}$) was produced using a Millipore water purification system. Unless otherwise stated, all chemicals were of analytical or HPLC grade and were used without further purification.

2.2. Preparation of PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$ and $\text{CN-PhC}_2\text{Cu/PhC}_2\text{Cu}$ heterointerface photocatalysts

PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$, and $\text{CN-PhC}_2\text{Cu/PhC}_2\text{Cu}$ heterointerface photocatalysts were prepared through a solution-phase copper acetylide formation method. For the reference PhC_2Cu sample, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.365 g) was dissolved in methanol (50 mL) under magnetic stirring, followed by the sequential addition of Et_3N (1.12 mL) and phenylacetylene (0.44 mL). The reaction mixture was maintained in a 70°C water bath under continuous stirring until a pale-yellow precipitate was formed. $\text{CN-PhC}_2\text{Cu}$ was synthesized using the same procedure, except that phenylacetylene was replaced by 4-ethynylbenzonitrile (0.136 g), yielding a yellow-brown flocculent precipitate.

For the preparation of $\text{CN-PhC}_2\text{Cu/PhC}_2\text{Cu}$ heterointerface photocatalysts, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.365 g), methanol (50 mL), and Et_3N (1.12 mL) were used under the same reaction conditions, while phenylacetylene and 4-ethynylbenzonitrile were simultaneously introduced according to predetermined molar ratios. The reaction was conducted at 70°C under continuous stirring, during which an orange-yellow precipitate gradually formed. All obtained solids were collected by centrifugation, washed repeatedly with ultrapure water and ethanol, dried overnight at 60°C , and ground into powders. A series of xCNPC samples was obtained by varying the molar percentage of 4-ethynylbenzonitrile in the total alkyne precursor feed, where x represents the molar percentage of 4-ethynylbenzonitrile. Among them, 75CNPC exhibited the optimal photocatalytic performance and was selected for subsequent investigations.

2.3. Preparation of physical mixture control sample

To distinguish the role of the in situ formed $\text{CN-PhC}_2\text{Cu/PhC}_2\text{Cu}$ heterointerface from simple physical mixing of the two components, a physical mixture control sample was prepared and denoted as 75CNPC-PM, where PM denotes a physical mixture. Specifically, 75 mg of $\text{CN-PhC}_2\text{Cu}$ and 25 mg of PhC_2Cu were mechanically mixed and thoroughly ground in an agate mortar until a visually homogeneous powder was obtained. The photocatalytic degradation performance of 75CNPC-PM toward DCF was evaluated under the same conditions as those used for the standard DCF degradation experiment and compared with that of the in situ synthesized 75CNPC.

2.4. Characterization

The as-prepared photocatalysts were systematically characterized using multiple analytical techniques, and the detailed instrument models are summarized in Table S1. The crystalline structures were analyzed by X-ray diffraction (XRD), while the surface functional groups were identified by Fourier-transform infrared spectroscopy (FTIR). The morphology, microstructure, and elemental distribution were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS). The surface elemental composition and chemical states were investigated by X-ray photoelectron spectroscopy (XPS), with all binding energies calibrated against the $\text{C } 1s$ peak at 284.8 eV. The optical absorption properties were evaluated by UV-visible diffuse reflectance spectroscopy (UV-vis DRS) using BaSO_4 as the reference. Steady-state photoluminescence, phosphorescence spectroscopy, and femtosecond transient absorption spectroscopy (fs-TAS) were used to investigate the excited-state behavior and charge-carrier dynamics of the photocatalysts. The photoelectrochemical properties, including transient photocurrent response, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV), were measured using a standard three-electrode system to evaluate charge separation, interfacial charge transfer, and electronic transfer behavior. Zeta potentials were measured at different pH values. Electron spin resonance/electron paramagnetic resonance spectroscopy (ESR/EPR) was employed to identify the reactive species generated during photocatalysis. UV-vis absorption and fluorescence spectroscopy were used to monitor the reactive-species probe experiments. Three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy was used to monitor changes in the fluorescent organic components of DCF solution before and after photocatalytic treatment. The residual DCF concentration was quantified by high-performance liquid chromatography (HPLC), and the transformation intermediates were identified by ultrahigh-performance liquid chromatography-quadrupole-Orbitrap high-resolution mass spectrometry (UHPLC-Q-Orbitrap MS). The toxicity of DCF and its identified transformation products was predicted using the ECOSAR and ProTox platforms. Total organic carbon (TOC) analysis was performed to evaluate the mineralization degree of DCF during photocatalytic degradation.

2.5. Photocatalytic degradation experiments

Photocatalytic degradation was performed using DCF as the target pollutant under irradiation from a 9 W visible-light LED source with a dominant wavelength of 455 nm. In a typical experiment, 20 mg of photocatalyst was dispersed in 50 mL of DCF solution ($10 \text{ mg}\cdot\text{L}^{-1}$) and magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium. The light source was then switched on, and aliquots were collected every 10 min. Each sample was filtered through a $0.45 \mu\text{m}$ membrane (ANPEL Laboratory Technologies Inc., Shanghai, China) before residual DCF concentration was measured. The photocatalytic reaction was terminated after 60 min.

Residual DCF concentration was quantified using high-performance liquid chromatography (HPLC, Shimadzu LC-20A, Japan). The analytical parameters were as follows: detection wavelength, 276 nm; injection volume, 20 μL ; mobile phase, methanol/0.2% formic acid aqueous solution (80:20, v/v); and flow rate, $1.0 \text{ mL}\cdot\text{min}^{-1}$. The removal efficiency of DCF was calculated using Eq. (1). The degradation kinetics were further analyzed by fitting the data to a pseudo-first-order kinetic model using Eq. (2).

$$R = (1 - C_t/C_0) \times 100\% \quad (1)$$

$$\ln(C_t/C_0) = -k_{\text{obs}} \times t \quad (2)$$

where C_0 and C_t represent the DCF concentrations ($\text{mg}\cdot\text{L}^{-1}$) at the initial

time and at reaction time t (min), respectively, and k_{obs} is the apparent reaction rate constant (min^{-1}). All photocatalytic experiments were performed in triplicate, and the results are reported as mean $\pm$ standard deviation. Additional photocatalytic tests were performed by varying the initial pH, pharmaceutical substrate, coexisting water constituents, and water matrix under otherwise identical reaction conditions. Recycling experiments were conducted for five consecutive cycles by recovering, washing, drying, and reusing the photocatalyst after each run.

2.6. Reactive-species quenching experiments

Reactive-species quenching experiments were conducted to evaluate the contributions of different reactive species during DCF degradation [17]. FFA ($10 \text{ mmol}\cdot\text{L}^{-1}$), TEMPOL ($10 \text{ mmol}\cdot\text{L}^{-1}$), KBrO_3 ($1 \text{ mmol}\cdot\text{L}^{-1}$), $\text{Na}_2\text{C}_2\text{O}_4$ ($10 \text{ mmol}\cdot\text{L}^{-1}$), and TBA ($10 \text{ mmol}\cdot\text{L}^{-1}$) were used to quench $^1\text{O}_2$, $\cdot\text{O}_2^-$, photogenerated electrons, holes, and $\cdot\text{OH}$, respectively. The inhibition rates were calculated using the following equations:

$$I_{e^-} = \frac{k_{e^-}}{k_{\text{app}}} \approx \frac{(k_{\text{app}} - k_{\text{KBrO}_3})}{k_{\text{app}}} \quad (3)$$

$$I_{h^+} = \frac{k_{h^+}}{k_{\text{app}}} \approx \frac{(k_{\text{app}} - k_{\text{Na}_2\text{C}_2\text{O}_4})}{k_{\text{app}}} \quad (4)$$

$$I_{^1\text{O}_2} = \frac{k_{^1\text{O}_2}}{k_{\text{app}}} \approx \frac{(k_{\text{app}} - k_{^1\text{O}_2})}{k_{\text{app}}} \quad (5)$$

$$I_{\cdot\text{O}_2^-} = \frac{k_{\cdot\text{O}_2^-}}{k_{\text{app}}} \approx \frac{(k_{\text{app}} - k_{\text{TEMPOL}})}{k_{\text{app}}} \quad (6)$$

$$I_{\cdot\text{OH}} = \frac{k_{\cdot\text{OH}}}{k_{\text{app}}} \approx \frac{(k_{\text{app}} - k_{\text{TBA}})}{k_{\text{app}}} \quad (7)$$

2.7. Reactive-species probe experiments

Reactive-species probe experiments were conducted to quantify $\cdot\text{O}_2^-$ and $^1\text{O}_2$. $\cdot\text{O}_2^-$ was quantified using NBT by monitoring its absorbance at 258 nm, whereas $^1\text{O}_2$ was quantified using DPBF by monitoring its absorbance at 418 nm under 520 nm irradiation. In each experiment, 10 mg of photocatalyst was dispersed in 50 mL of the corresponding probe solution and equilibrated in the dark for 30 min before irradiation. ROS amounts were determined from probe consumption using the corresponding stoichiometric relationships. H_2O_2 and $\cdot\text{OH}$ were additionally examined using iodometric and TPA fluorescence methods, respectively. Supplementary calibration, stoichiometric, and analytical details are provided in Text S1 of the Supporting Information.

2.8. $\text{H}_2\text{O}/\text{D}_2\text{O}$ comparative photocatalytic experiments

$\text{H}_2\text{O}/\text{D}_2\text{O}$ comparative photocatalytic experiments were conducted to assess the involvement of $^1\text{O}_2$ in DCF degradation. The experiments followed the standard photocatalytic degradation protocol, except that ultrapure water was replaced by D_2O as the reaction medium. The experiments in H_2O and D_2O were performed in parallel under otherwise identical conditions, and residual DCF concentrations were quantified by HPLC. The difference in degradation behavior between the two systems was used as supplementary evidence for the involvement of $^1\text{O}_2$, considering its prolonged lifetime in D_2O .

2.9. Theoretical calculations

All periodic density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) [21]. The exchange-correlation interaction was described using the Perdew-

Burke-Ernzerhof functional within the generalized gradient approximation (GGA) [22]. Core-valence interactions were treated using the projector augmented-wave (PAW) method [23,24]. Valence electrons were expanded in a plane-wave basis set with a cutoff energy of 520 eV, and the Brillouin zone was sampled using a $1 \times 1 \times 1$ Monkhorst-Pack k-point grid. The convergence criteria for electronic self-consistency and structural optimization were set to 1.0×10^{-6} eV and $0.03 \text{ eV}\cdot\text{\AA}^{-1}$, respectively. The DFT-D3 method was applied to account for van der Waals interactions. Molecular electrostatic potential (ESP) distributions, frontier molecular orbitals (FMOs), and dual Fukui functions were calculated based on Gaussian-optimized structure [25] and analyzed using Multiwfn [26] to evaluate electronic structures and reactive sites.

3. Results and discussion

3.1. Construction and interfacial coupling of the CN- $\text{PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ heterointerface

To construct a CN- $\text{PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ heterointerface with intimate contact and efficient electronic coupling, phenylacetylene and 4-ethynylbenzonitrile were used as organic ligand precursors to synthesize CN- $\text{PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ photocatalysts with different compositions through a one-step in situ route. Among these samples, 75CNPC showed the optimal photocatalytic performance. The synthesis involved precursor mixing, water-bath reaction, purification, drying, and grinding (Fig. 1a). During this process, the two copper acetylide structural units could form and assemble within the same reaction system, favoring intimate contact between CN- PhC_2Cu and PhC_2Cu .

SEM images show that PhC_2Cu exhibits relatively ordered one-dimensional nanowire/nanosheet assemblies with comparatively smooth surfaces, indicating a certain degree of ordered stacking (Fig. 1b). CN- PhC_2Cu is mainly composed of shorter intertwined nanowires with a looser overall architecture, suggesting that cyano introduction modifies the growth and stacking behavior of the original copper phenylacetylide framework (Fig. 1c). The 75CNPC composite retains one-dimensional nanowires as the basic building units, while the nanowires become more intertwined and assemble into denser bundle-like or cluster-like aggregates (Fig. 1d). The change in morphology therefore suggests altered growth and assembly behavior associated with the interaction between CN- PhC_2Cu and PhC_2Cu . EDS elemental mapping further shows uniform distributions of C, N, and Cu in 75CNPC, with homogeneous N distribution confirming successful incorporation of cyano-containing structural units into the composite (Fig. 1e).

XRD verifies the structural composition and composite characteristics of 75CNPC. As shown in Fig. 1f, PhC_2Cu shows distinct diffraction peaks at $2\theta = 6.0^\circ$ and 17.4° , assigned to the (100) and (010) planes of the aromatic copper acetylide framework, respectively, indicating ordered stacking [27]. The main diffraction peaks of CN- PhC_2Cu are located at approximately 10.5° and 15.8° , corresponding to the (200) and (300) planes, suggesting that cyano introduction alters molecular packing and crystal stacking [16]. The XRD pattern of 75CNPC retains the major diffraction features of both PhC_2Cu and CN- PhC_2Cu , supporting the coexistence and interfacial integration of the two structural units. Notably, slight peak shifts together with changes in peak intensity and shape, particularly around the (010) plane, indicate perturbation of the local crystal environment after composite formation and further support the interaction between CN- PhC_2Cu and PhC_2Cu .

FTIR spectra confirm preservation of the key functional groups and copper acetylide framework in the composite (Fig. 1g). PhC_2Cu exhibits a distinct band at approximately 1924 cm^{-1} , corresponding to the $\text{C}\equiv\text{C}-\text{Cu}$ stretching vibration, indicating formation of the copper phenylacetylide framework [28]. CN- PhC_2Cu retains the $\text{C}\equiv\text{C}-\text{Cu}$ feature and exhibits a new $\text{C}\equiv\text{N}$ stretching band at approximately 2229 cm^{-1} , confirming successful cyano incorporation. The weakened aromatic C-H vibration in the $600\text{--}800 \text{ cm}^{-1}$ region further suggests substitution of some aromatic hydrogen atoms by cyano groups.

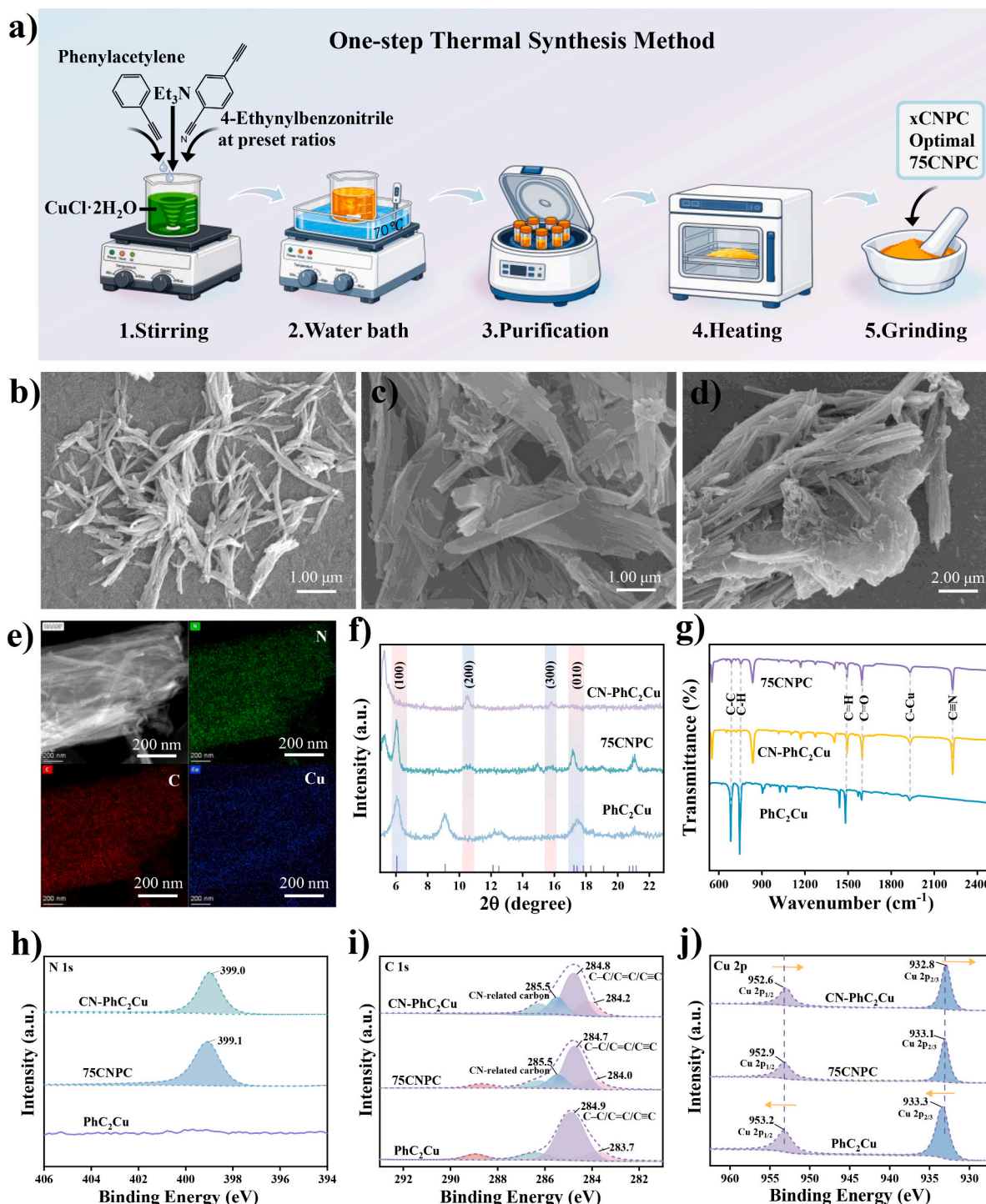


Fig. 1. Synthesis and structural characterization of $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ heterointerface photocatalysts. (a) Schematic illustration of the one-step in situ synthesis of xCNPC. SEM images of (b) PhC_2Cu , (c) $\text{CN-PhC}_2\text{Cu}$, and (d) 75CNPC. (e) Elemental mapping images of 75CNPC. (f) XRD patterns, (g) FTIR spectra, and high-resolution XPS spectra of (h) N 1s, (i) C 1s, and (j) Cu 2p for PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$, and 75CNPC.

75CNPC simultaneously retains the characteristic $\text{C}\equiv\text{C}-\text{Cu}$ and $\text{C}\equiv\text{N}$ bands, indicating that the main copper acetylide coordination framework remains intact and that cyano-containing units are stably incorporated into the composite.

XPS analysis supports the composition and interfacial electronic interactions of 75CNPC. In the survey spectra (Fig. S1), the N 1s signal appears only in $\text{CN-PhC}_2\text{Cu}$ and 75CNPC, and both show a $\text{C}\equiv\text{N}$ -related peak near 399 eV in the high-resolution N 1s spectra, confirming successful cyano incorporation and retention in the composite (Fig. 1h).

The C 1s spectra show an enhanced high-binding-energy component in $\text{CN-PhC}_2\text{Cu}$, indicating that the electron-withdrawing effect of $\text{C}\equiv\text{N}$ modifies the local electronic distribution of the aromatic copper acetylide framework. In 75CNPC, redistribution of C 1s peak position and intensity suggests interface-regulated electronic states in the carbon framework (Fig. 1i). Meanwhile, the Cu 2p peaks of 75CNPC are located between those of $\text{CN-PhC}_2\text{Cu}$ and PhC_2Cu (Fig. 1j), indicating a modified Cu electronic environment after composite formation. Together with the C 1s results, these changes support electronic modulation of the

$\text{C}\equiv\text{C}-\text{Cu}$ framework in 75CNPC [29].

The structural and surface analyses collectively support the formation of a CN-PhC₂Cu/PhC₂Cu heterointerface in 75CNPC. Importantly, cyano incorporation preserves the copper acetylide framework while altering the electronic environments of both the carbon skeleton and Cu coordination centers.

3.2. Band-structure-driven interfacial charge separation and transport

To elucidate how the CN-PhC₂Cu/PhC₂Cu heterointerface regulates photogenerated charge separation and transport, optical absorption, electrochemical characterization, and band-structure analyses were combined to examine interfacial charge migration.

UV-vis DRS results show that 75CNPC has an extended visible-light response. As shown in Fig. 2a, the absorption edges of PhC₂Cu, CN-

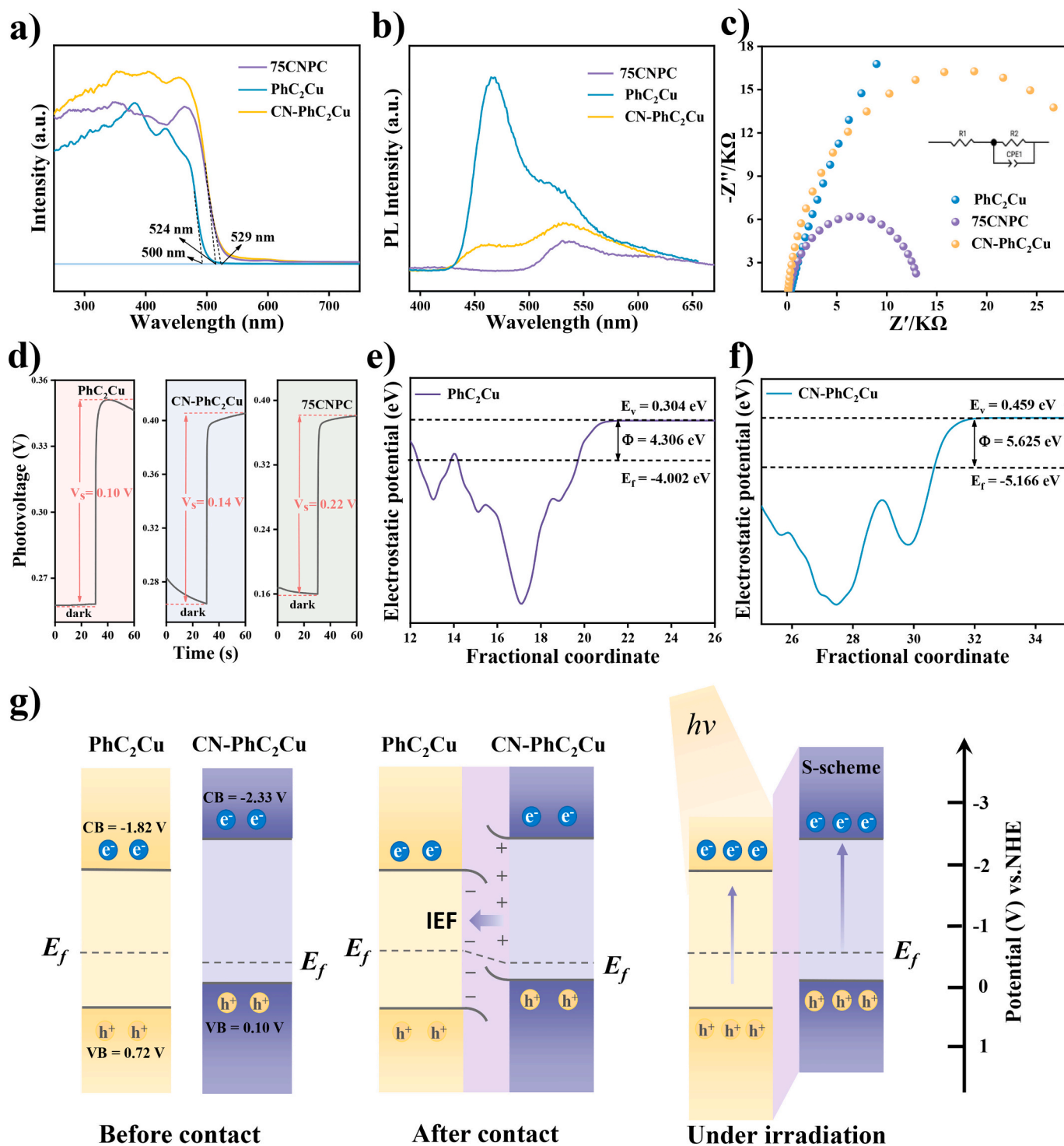


Fig. 2. Photoelectronic properties and proposed S-scheme charge-transfer mechanism of 75CNPC. (a) UV-vis DRS spectra. (b) Steady-state PL spectra. (c) EIS Nyquist plots. (d) Photovoltage responses of PhC₂Cu, CN-PhC₂Cu, and 75CNPC. Calculated electrostatic potential profiles and work functions of (e) PhC₂Cu and (f) CN-PhC₂Cu. (g) Schematic illustration of the S-scheme charge-transfer mechanism in 75CNPC.

PhC₂Cu, and 75CNPC are located at approximately 500, 524, and 529 nm, respectively. The pronounced red shift of CN-PhC₂Cu relative to PhC₂Cu indicates that cyano introduction modulates the electronic structure of the aromatic copper acetylide framework. The further broadened absorption edge of 75CNPC suggests that interfacial coupling also contributes to band-structure regulation and enhances visible-light utilization [17].

Steady-state PL spectroscopy was used to evaluate recombination of photogenerated electron-hole pairs. As shown in Fig. 2b, PhC₂Cu exhibits a strong emission signal, whereas 75CNPC shows markedly reduced PL intensity, indicating that construction of the heterointerface effectively suppresses radiative recombination of photogenerated carriers [30].

EIS and photovoltage measurements further support the improved interfacial charge transport and separation in 75CNPC. The Nyquist semicircle radius of 75CNPC is substantially smaller than those of PhC₂Cu and CN-PhC₂Cu (Fig. 2c), indicating the lowest charge-transfer resistance. Consistently, the photovoltage responses of PhC₂Cu, CN-PhC₂Cu, and 75CNPC are approximately 0.10, 0.14, and 0.22 V, respectively, following the order 75CNPC > CN-PhC₂Cu > PhC₂Cu (Fig. 2d). The lower interfacial impedance and stronger photovoltage response together demonstrate that photogenerated charges in 75CNPC can be more effectively separated and transported to the reaction interface [31].

CV results (Fig. S2) show that the conduction band/valence band (CB/VB) positions of PhC₂Cu are $-1.82/+0.72$ V versus NHE, while those of CN-PhC₂Cu are $-2.33/+0.10$ V versus NHE. Thus, CN-PhC₂Cu possesses a more negative conduction band and can provide stronger

reductive electrons, whereas PhC₂Cu has a relatively more positive valence-band position. The calculated work functions of PhC₂Cu and CN-PhC₂Cu are 4.306 and 5.625 eV, respectively (Figs. 2e and f), confirming an evident interfacial potential difference. The lower work function of PhC₂Cu implies a higher Fermi level; therefore, electrons tend to transfer from PhC₂Cu to CN-PhC₂Cu after contact until Fermi-level equilibration is reached. This charge redistribution is expected to generate a built-in electric field at the interface [32].

Based on the above band alignment and work-function difference, an S-scheme charge-migration mechanism is proposed for 75CNPC (Fig. 2g). Upon light irradiation, electrons in the conduction band of PhC₂Cu recombine with holes in the valence band of CN-PhC₂Cu at the interface, while the remaining electrons in the conduction band of CN-PhC₂Cu and holes in the valence band of PhC₂Cu are spatially separated [33].

3.3. Photocatalytic performance and aqueous matrix tolerance of CN-PhC₂Cu/PhC₂Cu

Based on the above structural and photoelectronic analyses, the photocatalytic performance of the CN-PhC₂Cu/PhC₂Cu samples was evaluated. As shown in Fig. 3a, the composite samples exhibited higher DCF removal than pristine PhC₂Cu and CN-PhC₂Cu, with 75CNPC achieving the highest removal efficiency of $95.2 \pm 3.9\%$ within 60 min. In comparison, the physical mixture 75CNPC-PM showed only $56.0 \pm 2.9\%$ DCF removal, with an apparent rate constant of $0.0137 \pm 0.0015 \text{ min}^{-1}$. Increasing the CN-PhC₂Cu proportion to 90CNPC did not further improve the degradation efficiency. These results suggest that the

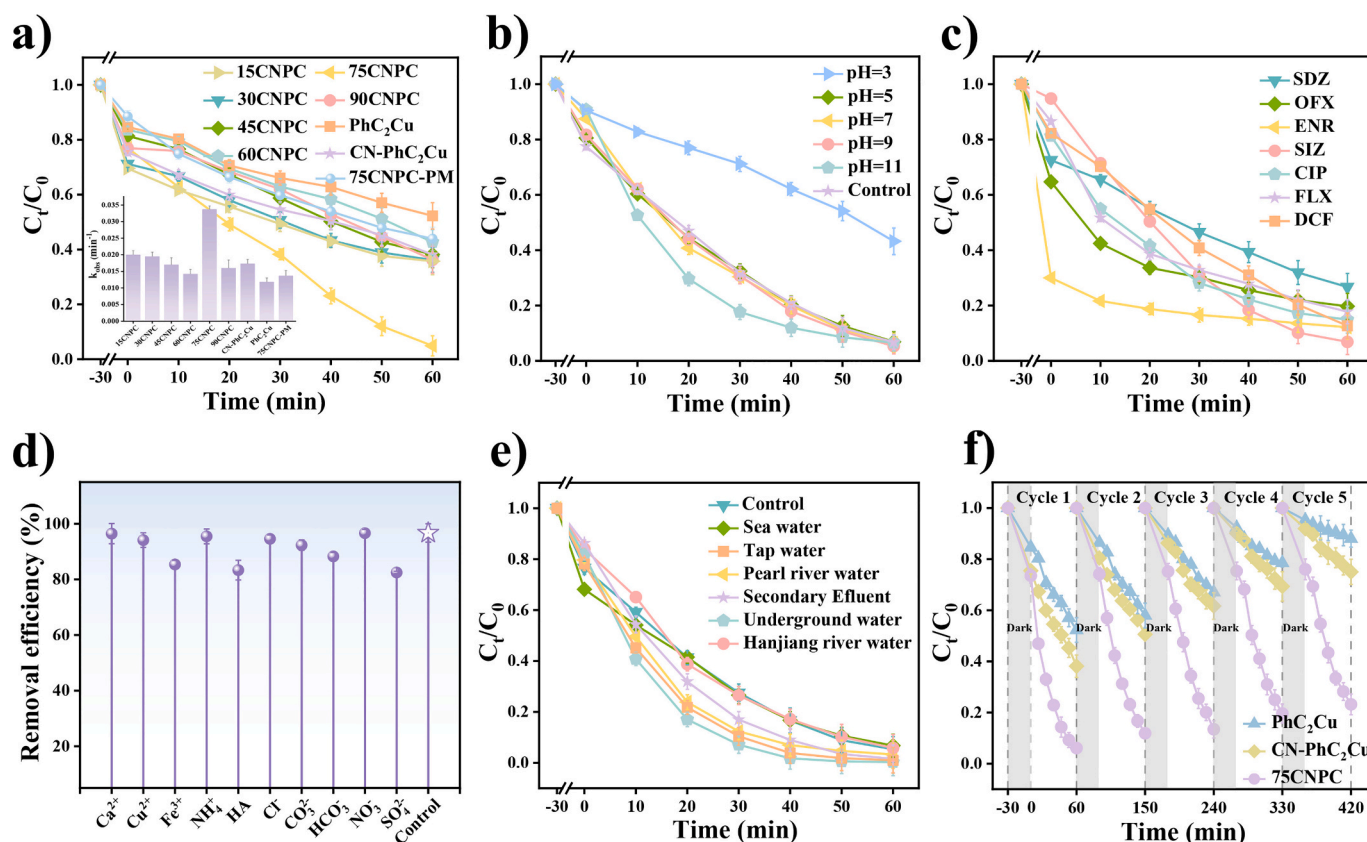


Fig. 3. Photocatalytic performance, aqueous-matrix tolerance, and reusability of 75CNPC. (a) DCF degradation over PhC₂Cu, CN-PhC₂Cu, xCNPC samples, and the physical mixture 75CNPC-PM under visible-light irradiation; inset: corresponding apparent rate constants. (b) Effect of initial pH on DCF degradation over 75CNPC. (c) Degradation of representative pharmaceutical contaminants over 75CNPC. (d) Effects of coexisting ions and humic acid (HA) on DCF degradation. (e) DCF degradation in different real water matrices. (f) Comparative recycling performance of PhC₂Cu, CN-PhC₂Cu, and 75CNPC over five consecutive DCF degradation cycles. Data are presented as mean $\pm$ standard deviation from three independent experiments ($n = 3$); error bars represent standard deviation and may be smaller than the symbols.

superior activity of 75CNPC may be associated with effective interfacial coupling established during the in situ synthesis, rather than simply with physical mixing or increasing the proportion of CN-PhC₂Cu. Therefore, 75CNPC was selected as the optimal composition for subsequent aqueous-matrix and mechanistic studies.

Solution pH significantly affects DCF degradation. As shown in Fig. 3b, 75CNPC maintains high degradation efficiency over pH 5–11, whereas the removal efficiency decreases to $56.8 \pm 4.4\%$ at pH 3. Combined with the pH-dependent distribution of DCF species and zeta-potential results in Fig. S3, DCF has a pK_a of approximately 4.35, and the point of zero charge of 75CNPC is approximately pH 3.3 [34]. Under neutral to alkaline conditions, both DCF and the catalyst surface tend to

be negatively charged, yet high activity is retained, suggesting that electrostatic attraction is not the dominant factor governing DCF removal. The main diffraction features of 75CNPC were largely retained after acidification (Fig. S4), indicating no obvious structural degradation under acidic conditions. Therefore, the reduced activity at pH 3 is more likely related to changes in DCF speciation and catalyst surface charge.

To assess the substrate scope of 75CNPC toward pharmaceutical contaminants, several representative drug molecules were selected for visible-light degradation. As shown in Fig. 3c, 75CNPC exhibits effective removal of pharmaceuticals with different structures, with all removal efficiencies exceeding 73% after 60 min and the highest reaching $93.1 \pm 4.4\%$. Although degradation efficiencies vary with molecular

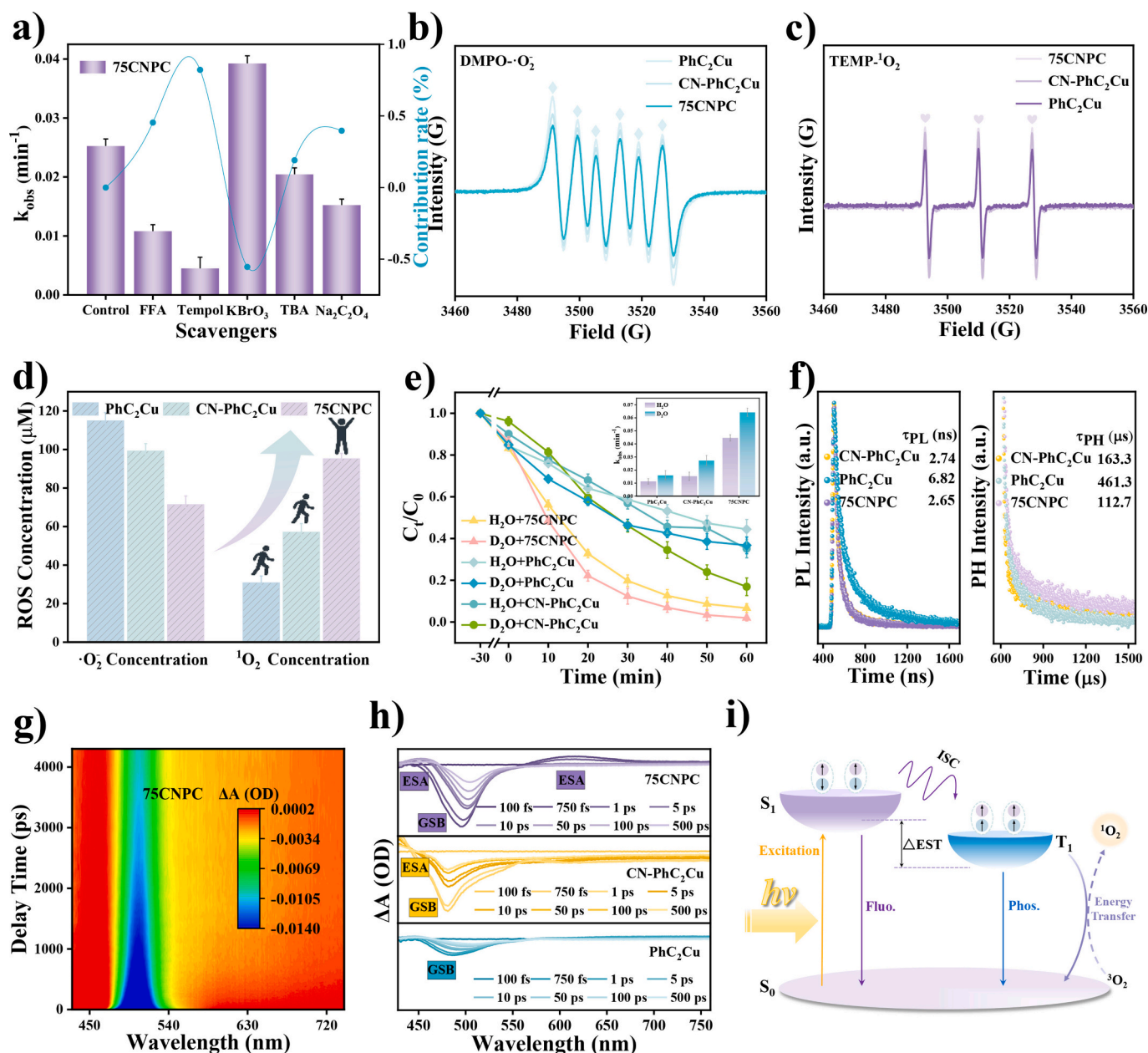


Fig. 4. Identification of ROS and triplet-state-related 1O_2 generation over 75CNPC. (a) Effects of different scavengers on DCF degradation over 75CNPC and the corresponding contribution rates of reactive species. (b) DMPO- $\cdot O_2^-$ and (c) TEMP- 1O_2 EPR spectra of PhC₂Cu, CN-PhC₂Cu, and 75CNPC. (d) Quantitative comparison of $\cdot O_2^-$ and 1O_2 generation over different samples. (e) DCF degradation over PhC₂Cu, CN-PhC₂Cu, and 75CNPC in H₂O and D₂O systems; the inset shows the corresponding apparent rate constants. (f) Time-resolved fluorescence and phosphorescence decay profiles. (g) Pseudo-color plot of femtosecond transient absorption spectra of 75CNPC. (h) Femtosecond transient absorption spectra at selected delay times. (i) Proposed triplet-state-mediated energy-transfer process for 1O_2 generation. Data in panels (a), (d), and (e), including the inset in panel (e), are presented as mean $\pm$ standard deviation from three independent experiments ($n = 3$). Error bars represent standard deviation and may be smaller than the symbols.

structure [35], substituent properties, and sensitivity to ROS, the overall results indicate that 75CNPC is not limited to DCF removal but has potential for treating multiple classes of pharmaceutical pollutants.

Coexisting-component experiments show that 75CNPC maintains high DCF removal in the presence of various ions and HA, with 60 min removal efficiencies remaining above 82% (Fig. 3d). Fe^{3+} , HA, HCO_3^- , and SO_4^{2-} exert relatively pronounced inhibitory effects. Fe^{3+} may competitively consume photogenerated electrons and weaken O_2 reduction to $\cdot\text{O}_2^-$ [36]; HA may reduce activity through light shielding, reactive-species scavenging, and occupation of catalyst surface sites [37]; and the inhibitory effects of HCO_3^- and SO_4^{2-} may be related to active-species quenching and competitive adsorption. These results indicate that 75CNPC maintains stable photocatalytic performance in the presence of common water constituents.

DCF degradation in actual water matrices is shown in Fig. 3e. In diverse real water samples, 75CNPC still achieves effective DCF degradation. Although inorganic salts, natural organic matter, and other background components may influence light absorption, surface adsorption, and ROS utilization, DCF removal in most systems approaches or exceeds 90% after 60 min, indicating its applicability to complex water matrices [38].

Recycling experiments were used to evaluate the reusability of 75CNPC. As shown in Fig. 3f, 75CNPC retains approximately 75%–80% DCF removal after five consecutive cycles, whereas PhC_2Cu and $\text{CN-PhC}_2\text{Cu}$ show less than 30% removal after the same cycles, indicating the superior reusability of 75CNPC. Moreover, post-cycling XRD (Fig. S5), SEM (Fig. S6), and FTIR (Fig. S7) analyses show no obvious changes in the crystal structure, morphology, or characteristic functional groups of 75CNPC, suggesting that its primary structure remains largely intact after repeated photocatalytic reactions [39].

3.4. Interfacial regulation of $\cdot\text{O}_2^-$ and $^1\text{O}_2$ generation pathways

To clarify the intrinsic reaction mechanism underlying efficient DCF degradation by 75CNPC, reactive-species scavenging experiments, EPR measurements, ROS quantification, $\text{H}_2\text{O}/\text{D}_2\text{O}$ comparative tests, atmosphere-controlled experiments, and excited-state characterizations were combined to analyze the ROS involved and the O_2 activation pathways [40]. As shown in Fig. 4a, TEMPOL and FFA, used as scavengers for $\cdot\text{O}_2^-$ and $^1\text{O}_2$, respectively, caused the most pronounced inhibition of DCF degradation among the tested scavengers, indicating that these two ROS made major contributions to the photocatalytic process. The weaker inhibition caused by TBA, KBrO_3 , and $\text{Na}_2\text{C}_2\text{O}_4$ suggests that $\cdot\text{OH}$, e^- , and h^+ are not dominant under the tested conditions.

EPR measurements and probe-based ROS quantification further clarified the ROS generation characteristics of the three samples. The $\text{DMPO}-\cdot\text{O}_2^-$ signal is strongest for PhC_2Cu , followed by $\text{CN-PhC}_2\text{Cu}$, whereas 75CNPC exhibits a weaker response (Fig. 4b). In contrast, 75CNPC shows the strongest $\text{TEMPOL}-^1\text{O}_2$ signal (Fig. 4c). Consistent with the EPR results, probe-based quantification shows the highest $\cdot\text{O}_2^-$ production for PhC_2Cu and markedly enhanced $^1\text{O}_2$ generation for 75CNPC (Fig. 4d). $\text{TEMPO}-\text{e}^-$ EPR further indicates stronger photogenerated-electron transfer behavior for PhC_2Cu , while 75CNPC retains detectable electron-transfer capability (Fig. S10). Taken together, these results indicate that heterointerface formation shifts the ROS distribution toward a $^1\text{O}_2$ -dominant O_2 activation pathway while retaining a secondary $\cdot\text{O}_2^-$ -related electron-transfer channel.

The involvement of $^1\text{O}_2$ was further supported by $\text{H}_2\text{O}/\text{D}_2\text{O}$ comparative experiments. Since the lifetime of $^1\text{O}_2$ is prolonged in D_2O relative to H_2O , changes in DCF degradation behavior between the two systems can provide supplementary evidence for $^1\text{O}_2$ participation [41]. As shown in Fig. 4e, DCF degradation was enhanced in D_2O , especially for 75CNPC, which exhibited the highest apparent rate constant. In addition, DCF degradation was strongly inhibited under N_2 atmosphere

but enhanced upon O_2 purging (Fig. S11), confirming that O_2 is a key precursor for ROS generation and pollutant oxidation. In DPBF-based $^1\text{O}_2$ probing experiments, TEMPOL and HDA were introduced as pathway-interference agents to compare changes in apparent $^1\text{O}_2$ generation (Figs. S12–S14) and to evaluate the relative contributions of $\cdot\text{O}_2^-$ -related conversion pathways and triplet-mediated energy-transfer pathways [42]. HDA caused a greater decrease in apparent $^1\text{O}_2$ generation than TEMPOL, suggesting that triplet-mediated energy transfer makes an important contribution to $^1\text{O}_2$ production in 75CNPC, while the $\cdot\text{O}_2^-$ -related conversion pathway is comparatively limited.

The enhanced $^1\text{O}_2$ production was further examined from the perspective of excited-state processes. The singlet-triplet energy gap (ΔEST) is an important energetic parameter associated with intersystem crossing and triplet-state formation [43]. As shown in Fig. S15, the ΔEST of 75CNPC is 0.314 eV, lower than those of PhC_2Cu and $\text{CN-PhC}_2\text{Cu}$, indicating that triplet-state formation is energetically more favorable in 75CNPC [1]. The reduced ΔEST of 75CNPC is more closely associated with heterointerface-induced excited-state modulation rather than with cyano substitution alone. ESP and frontier-orbital analyses show that the electron-withdrawing $\text{C}\equiv\text{N}$ group alters the electronic distribution of $\text{CN-PhC}_2\text{Cu}$, creating electronic asymmetry relative to PhC_2Cu (Fig. S16) [44]. Such electronic asymmetry provides an electronic basis for interfacial coupling and the subsequent modulation of excited-state behavior. Time-resolved fluorescence and phosphorescence analyses also show that the excited-state lifetimes of 75CNPC are shortened relative to PhC_2Cu (Fig. 4f), suggesting altered excited-state relaxation dynamics in 75CNPC. Femtosecond transient absorption spectroscopy was employed to further probe the ultrafast excited-state evolution of 75CNPC [45]. As shown in Figs. 4g and h, 75CNPC exhibits the strongest ground-state bleaching (GSB) response centered at approximately 500 nm (Fig. S17), together with distinct excited-state absorption (ESA) features near 440 and 600 nm. The enhanced GSB reflects a larger photoexcited-state population, while the retained ESA features indicate the coexistence of charge-related transient processes and triplet-state evolution after heterointerface formation. In particular, the pronounced ESA response around 440 nm, associated with S_1 -to- T_1 evolution, supports more effective triplet-state population in 75CNPC, consistent with the enhanced triplet-mediated energy-transfer pathway for $^1\text{O}_2$ generation.

Based on these results, an interface-regulated dual-channel O_2 activation mechanism is proposed for 75CNPC (Fig. 4i). Interfacial electronic coupling in $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ induces charge redistribution and excited-state modulation. The former preserves photogenerated electrons for reducing adsorbed O_2 to $\cdot\text{O}_2^-$, whereas the latter favors triplet-state formation and subsequent energy transfer from T_1 excitons to $^3\text{O}_2$, thereby enhancing $^1\text{O}_2$ generation [46]. Therefore, O_2 activation in 75CNPC follows a $^1\text{O}_2$ -dominant pathway assisted by $\cdot\text{O}_2^-$.

3.5. Theoretical analysis of interfacial charge redistribution and O_2 activation

Theoretical calculations further reveal the relationship between interfacial charge redistribution and O_2 activation in the $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ heterointerface. As shown in Figs. 5a–c, both PhC_2Cu and $\text{CN-PhC}_2\text{Cu}$ retain their aromatic copper acetylide coordination frameworks, and the composite forms a structurally matched heterointerface that provides a basis for interfacial electronic coupling [47]. Charge-density difference analysis shows pronounced electron accumulation and depletion near the interface; yellow isosurfaces represent electron accumulation, and blue isosurfaces represent electron depletion (Fig. 5d). Electrons mainly accumulate on the $\text{CN-PhC}_2\text{Cu}$ side and are depleted on the PhC_2Cu side, indicating that the cyano-functionalized unit acts as the electron-accepting region after interfacial coupling. Bader charge analysis gives a net transfer of approximately 0.185 e from PhC_2Cu to $\text{CN-PhC}_2\text{Cu}$, in agreement with the charge-density difference maps. This result confirms ground-state interfacial charge

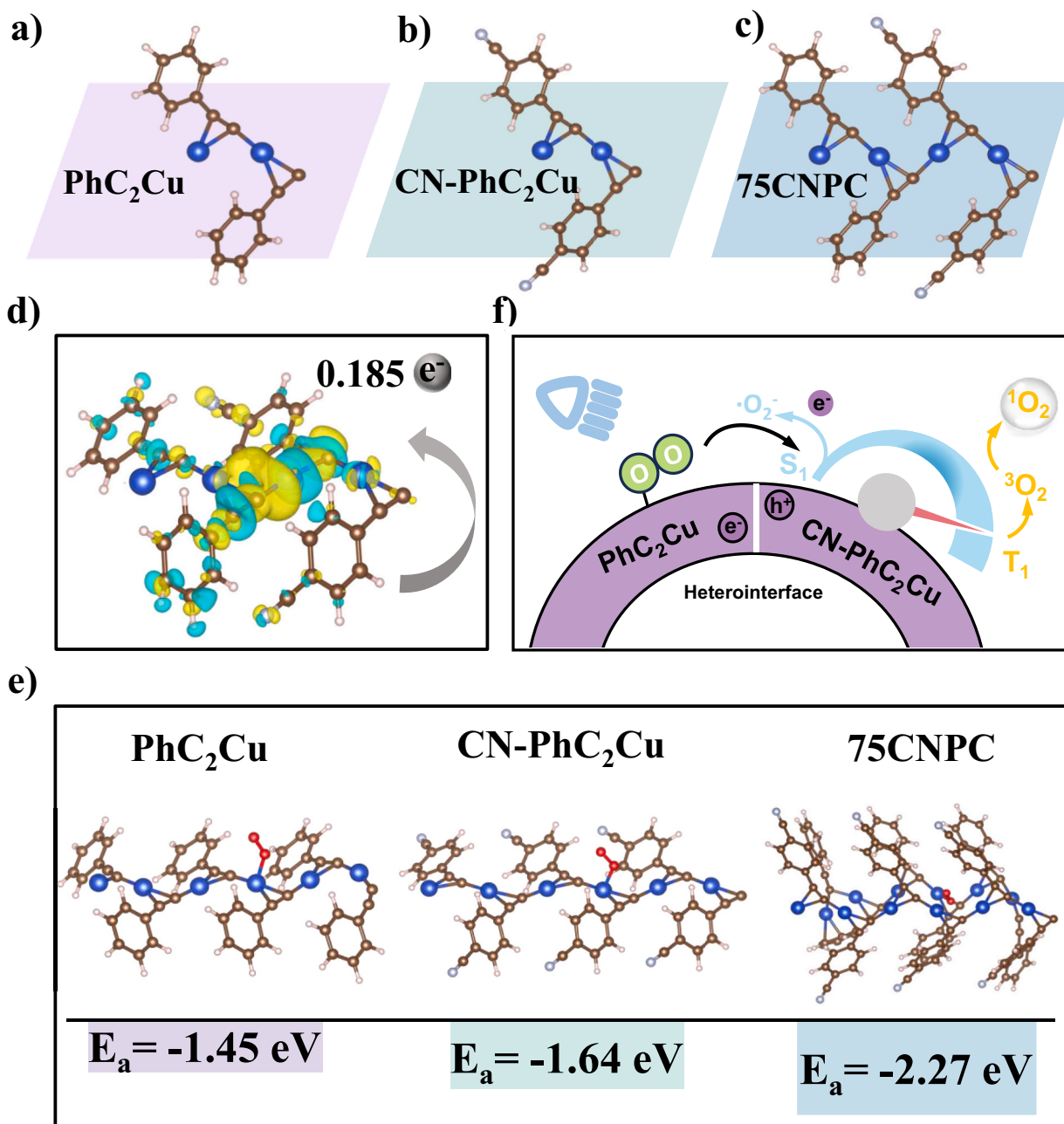


Fig. 5. DFT analysis of interfacial charge redistribution and O₂ activation in 75CNPC. (a–c) Optimized structures of PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$ and 75CNPC . (d) Charge density difference and Bader charge transfer across the $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ interface. Yellow and blue isosurfaces denote electron accumulation and depletion, respectively. (e) O₂ adsorption configurations and adsorption energies on PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$ and 75CNPC . (f) Schematic illustration of interface-regulated O₂ activation and $\cdot\text{O}_2^-/{}^1\text{O}_2$ generation over 75CNPC . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

redistribution, which is favorable for establishing a local built-in electric field and provides a more suitable electronic environment for O₂ adsorption and activation.

Interfacial charge redistribution further affects O₂ adsorption and activation. O₂ adsorption energy is commonly used to evaluate the binding strength between molecular oxygen and catalyst surfaces; a more negative value indicates a more exothermic adsorption process and stronger O₂-surface interaction [48]. In photocatalytic O₂ activation, moderately enhanced O₂ adsorption can improve surface O₂ enrichment and increase the probability of interaction with photo-generated electrons or interfacial active sites. As shown in Fig. 5e, the O₂ adsorption energies of PhC_2Cu , $\text{CN-PhC}_2\text{Cu}$, and 75CNPC are -1.45 ,

-1.64 , and -2.27 eV , respectively, indicating that 75CNPC binds O₂ most strongly. This result demonstrates that the composite interface does not merely combine the intrinsic adsorption capacities of the two parent components; instead, interfacial charge migration retunes the electronic state of local active sites, leading to more favorable O₂ binding at the interface. Together with the charge-density difference and Bader charge results, the electronic redistribution at the $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ interface provides a more favorable electronic environment for O₂ adsorption and subsequent electron interaction, thereby supporting the generation of $\cdot\text{O}_2^-$ and ${}^1\text{O}_2$ -related active species.

Accordingly, Fig. 5f summarizes the interface-induced O₂ activation process. The $\text{CN-PhC}_2\text{Cu}/\text{PhC}_2\text{Cu}$ heterointerface promotes directional

charge separation and allows electrons to reduce adsorbed O_2 to $\cdot O_2^-$. At the same time, interface-regulated excited-state processes support triplet-energy transfer from the catalyst to 3O_2 , producing 1O_2 [47]. The theoretical results therefore provide an electronic-structure basis for the experimentally observed $\cdot O_2^-$ / 1O_2 -mediated ROS pathway regulation in 75CNPC.

3.6. Transformation pathways and toxicity evolution of DCF

After identifying $\cdot O_2^-$ and 1O_2 as the major ROS involved in the 75CNPC system, the reactive sites, transformation pathways, and potential toxicity changes of DCF were further investigated. Frontier orbital and molecular electrostatic potential analyses were first used to predict reactive regions in DCF. As shown in Figs. 6a and b, the highest

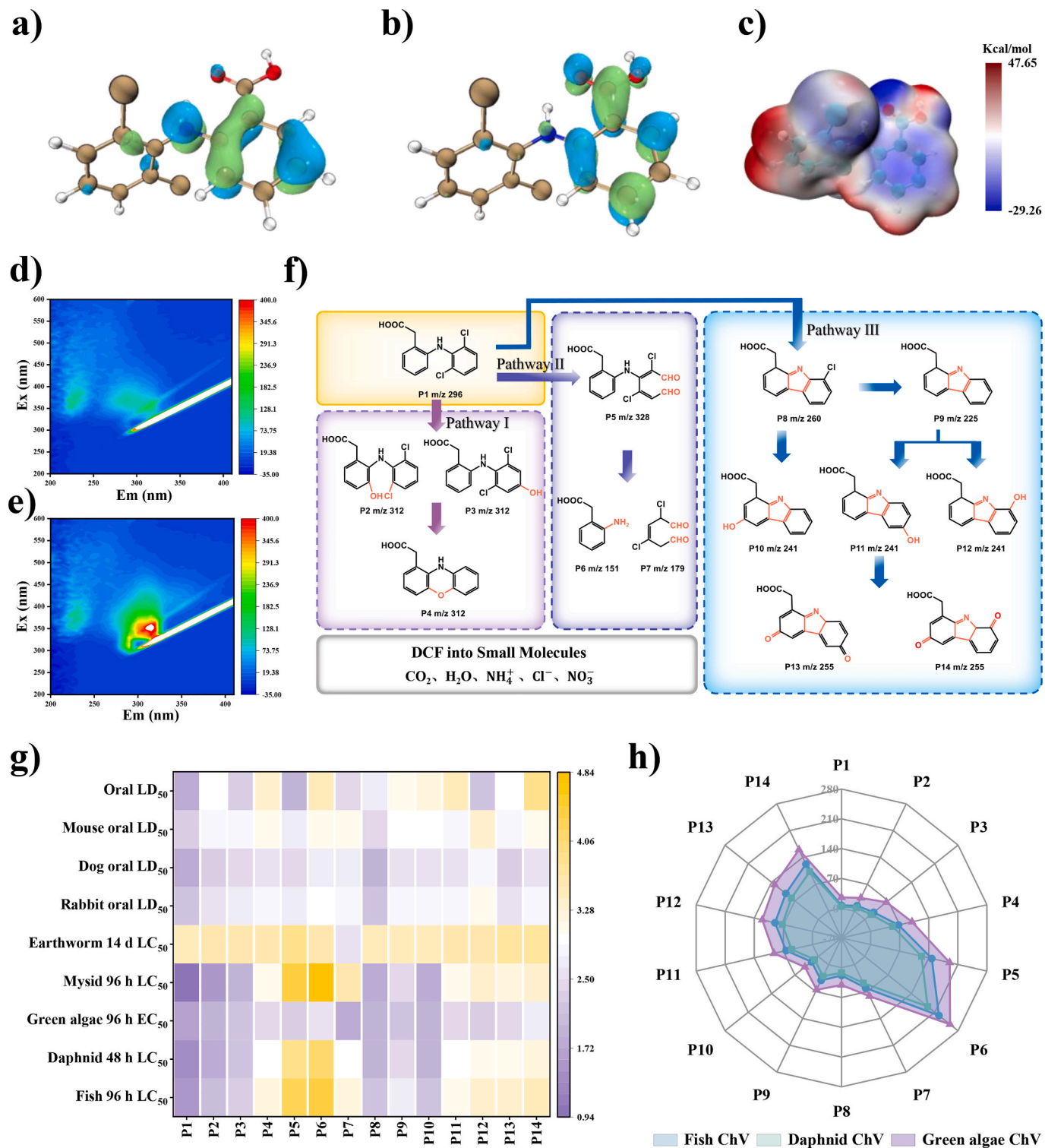


Fig. 6. Reactive sites, transformation pathways and toxicity evolution of DCF in the 75CNPC system. (a) HOMO and (b) LUMO orbital maps of DCF. (c) ESP mapping distribution of DCF. Three-dimensional fluorescence spectra of DCF solution (d) before and (e) after photocatalytic degradation over 75CNPC. (f) Proposed DCF degradation pathways based on LC-MS analysis. Predicted (g) acute and (h) chronic toxicity profiles of DCF and its identified transformation products.

occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of DCF are mainly distributed over the aromatic rings, amine-bridged structure, and carboxyl-adjacent region, indicating that these sites have high electron-transfer activity and are prone to participate in photocatalytic redox reactions [49]. Electrostatic potential (ESP) results show distinct electron-density differences around the aromatic rings, chlorinated phenyl ring, and N-containing bridge (Fig. 6c), with electron-rich regions more susceptible to attack by $^1\text{O}_2$, $\cdot\text{O}_2^-$, and photogenerated holes. Fukui-function analysis (Fig. S18) further indicates that the amine-bridged N atom, aromatic carbon sites, chlorinated substituent region, and carboxyl-adjacent positions exhibit high reactivity, suggesting that these sites are more likely to undergo electrophilic oxidation, radical attack, or bond cleavage. Therefore, initial DCF transformation may preferentially occur through aromatic hydroxylation, C—Cl bond activation, C—N bond cleavage, and rearrangement near the carboxyl group [50].

Three-dimensional fluorescence spectroscopy provides a qualitative view of structural changes in the solution [51]. As shown in Figs. 6d and e, the initial DCF solution exhibits strong fluorescence, indicating the presence of aromatic organic components with conjugated structures. After photocatalytic treatment with 75CNPC, the intensities of the major fluorescence regions decrease markedly, accompanied by changes in peak position and distribution range. This indicates destruction of the conjugated aromatic structure of DCF and gradual conversion of part of the larger molecular structure into small-molecule intermediates with weaker fluorescence response [52].

LC-MS analysis (Fig. S18) was then used to identify intermediates and infer transformation routes [50]. Based on the structural characteristics of the detected intermediates and the ROS identification results, DCF transformation in the 75CNPC system may involve three main reaction tendencies: radical-involved initial activation, framework fragmentation, and $^1\text{O}_2$ -involved selective progressive oxidation (Fig. 6f).

Pathway I may involve aromatic hydroxylation, followed by dechlorination-related transformation and intramolecular cyclization, indicating early-stage structural modification involving radicals. Combined with the ROS analysis, this process is mainly associated with $\cdot\text{O}_2^-$ -initiated oxidation and may involve minor contributions from $\cdot\text{OH}$. Pathway II shows more pronounced radical-driven fragmentation: DCF undergoes further dechlorination-related transformation, enhanced oxidation, C—N bond cleavage, and formation of low-molecular-weight fragments, reflecting the important role of radical processes in parent-framework destruction. By contrast, Pathway III is more consistent with $^1\text{O}_2$ -dominated non-radical selective deep oxidation [53]. In this pathway, the main DCF framework is retained over a longer stage and preferentially undergoes cyclization, stepwise oxidation, hydroxylation, and subsequent carbonylation/quinone-like oxidation. Such relatively directional and progressive structural evolution agrees with the selective attack behavior characteristic of $^1\text{O}_2$ -mediated oxidation. These results suggest that the 75CNPC regulates DCF degradation by modulating both ROS contributions and molecular transformation routes. The identified intermediates indicate a multipath oxidation process in the 75CNPC system, with $\cdot\text{O}_2^-$ mainly participating in initial activation and framework cleavage, while $^1\text{O}_2$ contributes to selective deep oxidation. The coexistence of radical and non-radical pathways during DCF transformation has also been reported in other interfacial catalytic systems [54].

Finally, toxicity prediction (Tables S2 and S3) and mung bean cultivation experiments were used to assess the potential risk associated with DCF transformation [55]. Acute toxicity heatmaps (Fig. 6g) and chronic toxicity radar plots (Fig. 6h) show an overall decrease in the toxicity of DCF and its intermediates as the photocatalytic reaction proceeds, indicating that the $\cdot\text{O}_2^-/^1\text{O}_2$ cooperative oxidation process induced by 75CNPC not only promotes removal of the parent DCF molecule but also helps reduce the potential risk of degradation products [56]. Mung bean cultivation experiments further support this result: the

original DCF solution markedly inhibits germination and seedling elongation (Fig. S20), whereas this inhibition is significantly weakened after photocatalytic treatment by 75CNPC, with plant growth approaching that of the blank control. These results demonstrate that 75CNPC can not only efficiently degrade DCF but also mitigate the potential ecotoxicity of the treated system [57].

4. Conclusions

This study constructed a CN-PhC₂Cu/PhC₂Cu heterointerface through a one-step in situ strategy and demonstrated efficient visible-light-driven DCF degradation. The results show that cyano functionalization and heterointerface coupling reconstruct the local electronic structure of the copper acetylide framework, promote S-scheme charge migration, suppress carrier recombination, and enhance O₂ adsorption and activation. The optimized 75CNPC exhibits high degradation efficiency and retains appreciable activity in different aqueous matrices and during repeated use. Mechanistic analyses reveal that interfacial electronic coupling regulates O₂ activation through two coupled processes: charge redistribution and excited-state modulation. The former preserves reductive electrons for one-electron reduction of O₂ to $\cdot\text{O}_2^-$, whereas the latter favors triplet-state formation and subsequent energy transfer from T₁ excitons to $^3\text{O}_2$, thereby promoting $^1\text{O}_2$ generation. Consequently, DCF degradation over 75CNPC is governed by a $^1\text{O}_2$ -dominant pathway assisted by $\cdot\text{O}_2^-$, indicating interface-regulated modulation of O₂ activation. Theoretical calculations further confirm directional interfacial charge redistribution from PhC₂Cu to CN-PhC₂Cu, which favors O₂ capture and subsequent activation. LC-MS product analysis and toxicity assessment indicate that DCF undergoes initial activation, framework fragmentation, and selective progressive oxidation, accompanied by removal of the parent pollutant and reduced predicted toxicity. Overall, this work shows that CN-PhC₂Cu/PhC₂Cu interfacial engineering can regulate O₂ activation and ROS generation pathways in organometallic photocatalytic systems.

CRedit authorship contribution statement

Bingbing Liu: Writing – original draft, Validation, Investigation, Formal analysis, Conceptualization. **Jin Wu:** Methodology. **Li Tang:** Software, Formal analysis. **Ping Chen:** Software, Resources, Methodology, Formal analysis. **Haiyu Li:** Validation, Resources, Methodology. **Fengyuan Zhang:** Software, Resources, Methodology, Formal analysis. **Yanfang Wang:** Validation, Supervision. **Yunshuang He:** Validation, Resources, Methodology. **Zili Lin:** Methodology. **Wenyang Lv:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **Guoguang Liu:** Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2026.141544>.

Data availability

Data will be made available on request.

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