

Coordination-Defined Ionic Cococrystals Drive Electronic Structure Engineering in Ionic Carbon Nitrides for High-Performance H₂O₂ Photosynthesis

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Abstract

Ionic cocrystal (ICC) precursors have emerged as promising platforms for directing the formation of ionic carbon nitrides through precursor structural organization, yet whether their molecular coordination environments can independently govern the electronic structure of the resulting photocatalysts remains largely unexplored. Here, we show that a crystalline urea-LiCl ICC, featuring discrete Li-carbonyl coordination motifs rather than graphitic-like layered assemblies, serves as a coordination-defined precursor that directs framework evolution to produce poly(heptazine imide) (PHI) with a tailored electronic structure. Incorporation of NaCl into this precursor yields an ionic carbon nitride (ULiNa) exhibiting an apparent quantum yield of 89% at 410 nm for photocatalytic H_2O_2 production, representing the highest benchmarked activity among state-of-the-art photocatalysts for H_2O_2 synthesis, while requiring 12-fold less inorganic salt than conventional ionothermal methods. Composition-matched control materials produced through equilibrium ionothermal synthesis, post-synthetic salt treatment, and cation exchange nevertheless exhibit much lower activities despite possessing similar alkali-metal compositions. Structural characterization confirms that ULiNa preserves the conventional PHI framework, whereas X-ray spectroscopic analyses reveal systematic modifications to its electronic structure arising from Li-directed precursor coordination. Electrochemical measurements demonstrate enhanced oxygen reduction kinetics while maintaining the selective two-electron pathway to H_2O_2 , and density functional theory calculations show strengthened O_2 adsorption together with stabilization of key oxygen reduction intermediates. Overall, these results demonstrate that molecular coordination environments encoded within ICC precursors can direct the electronic structure and catalytic function of ionic carbon nitrides without altering their fundamental framework, establishing precursor coordination chemistry as a complementary design principle to structural templating for engineering polymeric photocatalysts.

1. Introduction

Solar-driven conversion of molecular oxygen into hydrogen peroxide (H_2O_2) offers an attractive route toward decentralized chemical production.^{1, 2} However, achieving high efficiency in particulate photocatalytic systems remains intrinsically challenging because the desired two-electron oxygen reduction (2e^- ORR) pathway competes with both 4e^- reduction to water and undesired peroxide decomposition.^{3, 4, 5, 6} Consequently, the ability of a photocatalyst to regulate charge distribution, stabilize reaction intermediates, and promote selective oxygen reduction is often more critical than maximizing light absorption or surface area alone.⁷

Polymeric carbon nitrides have emerged as promising metal-free photocatalysts owing to their tunable electronic structures, chemical robustness, and earth-abundant composition.^{8, 9, 10} Among them, ionic carbon nitrides, particularly poly(heptazine imides) (PHIs), incorporate charge-compensating alkali-metal cations that influence the electrostatic landscape of the semiconductor, thereby affecting charge transport, adsorption energetics, and catalytic selectivity.^{11, 12, 13, 14} Conventional synthetic strategies

rely primarily on equilibrium-driven ionothermal synthesis or post-synthetic ion exchange, in which cation incorporation occurs during or after framework formation under thermodynamic control.^{15, 16, 17, 18, 19} Although these approaches enable compositional tuning, they provide limited control over how precursor-level coordination influences framework evolution and the resulting electronic structure.^{20, 21} Establishing this relationship remains a central challenge in the rational design of ionic carbon nitride photocatalysts.

Crystalline organic-inorganic ionic cocrystals (ICCs) have recently emerged as an alternative precursor platform for ionic carbon nitride synthesis. In layered ICCs, graphitic-like molecular organization can be partially retained during condensation, enabling topotactic transformation and precursor-directed ionic organization within the resulting PHI framework.^{22, 23} Whether the resulting photocatalytic properties arise primarily from inherited structural organization or from the underlying coordination chemistry that governs framework evolution, however, remains unresolved. Addressing this question requires precursor systems that preserve well-defined coordination environments while eliminating extended layered architectures capable of structural templating.

Here, we address this question using a fundamentally different ICC precursor based on a crystalline urea-LiCl assembly. Unlike previously reported layered ICCs, this precursor consists of discrete molecular coordination environments in which Li^+ is coordinated by carbonyl oxygen atoms without graphitic-like structural organization capable of directing topotactic framework evolution. Incorporation of NaCl followed by thermal condensation yields an ionic carbon nitride, denoted ULiNa, with an apparent quantum yield of 89% at 410 nm, the highest among benchmarked state-of-the-art photocatalysts for H_2O_2 production. Through extensive control experiments, cation-exchange studies, spectroscopy, electrochemical measurements, and density functional theory calculations, we demonstrate that the exceptional photocatalytic performance cannot be explained by alkali-metal content, crystallinity, or surface area alone. Instead, precursor coordination chemistry governs framework evolution, producing an electronic structure that promotes oxygen activation and highly efficient 2e^- ORR. These findings establish that molecular coordination environments encoded before polymerization can determine the electronic structure and catalytic function of ionic carbon nitrides, extending ICC chemistry beyond structural templating toward coordination-directed materials design.

2. Results and discussion

Photocatalytic H_2O_2 production on ionic cocrystal-derived ionic carbon nitrides

Ball milling of stoichiometric amounts of urea and LiCl produced a crystalline precursor phase (ULi-P) with diffraction features distinct from those of pristine urea and LiCl, confirming the formation of a new molecular assembly rather than a physical mixture (Figure S1). To gain insight into its coordination environment, a structural model derived from the reported urea-LiI²⁴ ICC structure was constructed through halide substitution followed by DFT relaxation. The optimized structure reveals Li^+ centers predominantly coordinated by carbonyl oxygen atoms within a discrete molecular assembly lacking

extended layered order (Fig. 1a). Although the simulated diffraction pattern does not reproduce the experimental profile exactly (Figure S1), it captures the complex reflection distribution characteristic of the ULi-P phase, supporting the formation of a coordination-defined crystalline precursor. Unlike the layered cyanuric acid-based ICCs reported previously, ULi-P does not possess an obvious graphitic-like structural motif capable of direct topotactic transfer to the final PHI framework. Instead, it provides a model system for evaluating how precursor coordination chemistry governs framework evolution during polymerization. ULi-P was then thermally condensed at 600°C for 4 h under N₂ (Fig. 1a), yielding a yellowish-orange ionic carbon nitride denoted ULi-11 (urea:LiCl = 1:1). Photocatalytic H₂O₂ evolution was evaluated in an O₂-saturated aqueous glycerol solution (10 wt%) under monochromatic 410 nm irradiation without cocatalysts. Among the ULi series, a urea:LiCl molar ratio of 2:0.5 afforded the highest H₂O₂ concentration of 11.4 mM (Figure S2), whereas further increasing the LiCl content decreased the activity.

To probe the role of precursor coordination chemistry, analogous urea-based systems incorporating NaCl, KCl, and CsCl were synthesized under identical conditions. In contrast to LiCl, none of these alkali metal chlorides produced crystalline products after thermal treatment. This behavior differs from conventional melamine-based ionothermal synthesis, in which NaCl, KCl, and CsCl generate crystalline PHI salts through direct solid-state condensation.²⁵ The contrasting outcomes demonstrate that successful framework formation depends not on the identity of the alkali metal, but on its coordination chemistry with the molecular precursor. We therefore attribute the unique behavior of the ULi precursor to the strong coordination between Li⁺ and the carbonyl oxygen atoms of urea prior to polymerization. Such precursor-level coordination is proposed to stabilize key condensation intermediates, regulate framework evolution, and establish the electronic structure responsible for the superior photocatalytic performance.

Motivated by the unique role of Li-O coordination, dual-cation systems were constructed by introducing NaCl into the urea-LiCl precursor assembly (urea:LiCl:NaCl molar ratio = 2:0.5:0.5). Thermal polymerization under identical conditions yielded a yellowish-green material, denoted ULiNa (Fig. 1a). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis confirmed the coexistence of Li (1.2 wt%) and Na (5.3 wt%) within the framework (Table S1), while powder X-ray diffraction (PXRD) revealed a crystalline structure closely resembling that of conventional NaPHI (Fig. 1b). ULiNa exhibited a 3.1-fold enhancement in photocatalytic H₂O₂ production relative to NaPHI and a further 95% increase compared with ULi (Fig. 1c).

Varying either the LiCl/NaCl ratio or the urea content resulted in diminished activity, indicating that efficient photocatalysis requires an optimized interplay between precursor coordination chemistry and dual-cation incorporation during framework formation. Systematic optimization identified a polymerization temperature of 600°C and a reaction time of 4 h as the optimum conditions for maximizing H₂O₂ production (Figure S3 and S4). The optimized ULiNa photocatalyst exhibited excellent operational stability, maintaining its activity over five consecutive photocatalytic cycles without

measurable performance loss (Fig. 1d). Post-reaction structural characterization revealed no discernible changes apart from partial proton exchange (Figure S5), demonstrating the robustness of the PHI framework under photocatalytic conditions.

To evaluate the broader applicability of this coordination-directed synthetic strategy, additional dual-cation materials were prepared by replacing NaCl with other alkali metal chlorides. In contrast to the corresponding single-cation systems, all dual-cation precursor assemblies successfully produced crystalline PHI materials under similar polymerization conditions, further highlighting the pivotal role of Li-centered precursor coordination in directing framework formation (Figure S6). Nevertheless, photocatalytic performance depended strongly on the identity of the secondary cation, following the trend ULiNa > ULiK > ULiRb > ULiCs (Fig. 1e). ICP-OES analysis revealed comparable Li contents for ULiNa, ULiRb, and ULiCs (1.0–1.2 wt%) despite their varying activities, whereas ULiK outperformed both ULiRb and ULiCs despite containing the lowest Li concentration (0.5 wt%) (Table S2). Likewise, no correlation was observed between activity and total alkali-metal content, as the Cs- and Rb-containing materials incorporated higher alkali ion loadings than ULiNa yet displayed inferior performance. These observations demonstrate that photocatalytic activity is governed neither by Li concentration nor by the overall alkali-metal content. Instead, they suggest that the secondary cation modulates the electronic structure established through Li-directed precursor coordination, ultimately determining photocatalytic performance.

To determine whether the exceptional activity of ULiNa originates from its unique precursor architecture rather than its elemental composition, a series of reference materials was synthesized using established preparation routes. These included an ionothermally prepared PHI obtained directly from urea, LiCl, and NaCl in a molten-salt medium (U-PHI-MS), a material generated by post-treatment of preformed urea-derived carbon nitride with LiCl/NaCl salts (U-PHI-2S), and a Li-exchanged NaPHI analogue (Li-NaPHI) (Scheme S1; Figure S7). Despite incorporating the same chemical components, all three reference catalysts showed much lower activities than ULiNa (Fig. 1f). H₂O₂ concentrations remained below 2 mM for both U-PHI-MS and U-PHI-2S, while Li-NaPHI achieved 12.3 mM. Under identical conditions, ULiNa produced 25.6 mM H₂O₂, outperforming all conventionally prepared analogues. These differences cannot be explained by variations in alkali-metal composition. ICP-OES measurements revealed comparable Li and Na contents for ULiNa (Li = 1.2 wt%, Na = 5.3 wt%), U-PHI-2S (Li = 1.2 wt%, Na = 5.1 wt%), and U-PHI-MS (Li = 0.9 wt%, Na = 5.3 wt%) (Table S1), despite their different photocatalytic activities. Furthermore, Li-NaPHI contains twice the Li content of ULiNa, yet exhibits only half of its activity. These comparisons demonstrate that neither alkali-metal loading nor the mere presence of Li and Na within the PHI framework is sufficient to account for the observed photocatalytic performance. Instead, they highlight the importance of how the alkali-metal ions are incorporated during framework formation. In ULiNa, condensation proceeds from a crystalline urea-LiCl precursor in which Li⁺ is preorganized through coordination to carbonyl oxygen atoms prior to polymerization. In contrast, U-PHI-MS is synthesized under conventional ionothermal conditions, where alkali-metal incorporation occurs under equilibrium molten-salt conditions, while U-PHI-2S and Li-NaPHI introduce alkali-metal ions only

after the framework has formed. Despite employing the same Li/Na chemistry, none of these conventional approaches reproduces the activity of ULiNa, suggesting that the precursor coordination environment, rather than the final alkali-metal composition, governs framework evolution and establishes the electronic structure responsible for efficient photocatalysis. Beyond its superior photocatalytic performance, ULiNa is synthesized with a 5-fold higher product yield while requiring 12-fold less inorganic salt than conventional molten-salt synthesis (0.42 versus 5.0 g salt g⁻¹ precursor; Table S3). These practical advantages further illustrate the potential of coordination-directed synthesis as an alternative to conventional equilibrium-driven ion incorporation for preparing ionic carbon nitrides.

Next, we evaluated the wavelength-dependent photocatalytic performance of ULiNa to assess its efficiency across the visible spectrum. Under all irradiation conditions, ULiNa outperformed both NaPHI and ULi-41, demonstrating superior H₂O₂ generation rates (Figure S8). Apparent quantum yields (AQYs) of 89% at 410 nm and 31% at 465 nm were obtained (Fig. 1g), representing the highest benchmarked values among state-of-the-art carbon nitride and non-carbon nitride photocatalysts for H₂O₂ synthesis (Table S4). To examine the intrinsic ORR activity, ULiNa and NaPHI were investigated using rotating ring-disk electrode measurements in O₂-saturated 0.2 M Na₂SO₄ electrolyte. ULiNa exhibited 40% higher cathodic current densities over the investigated rotation range (Figure S9), indicating faster ORR kinetics. Despite this enhancement, both materials displayed electron transfer numbers close to 2, confirming that oxygen reduction proceeds through the selective 2e⁻ pathway to H₂O₂ while effectively suppressing the competing 4e⁻ reduction route to water. Evidence for oxygen activation was obtained from electron paramagnetic resonance spectroscopy using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent. No signal was detected in the dark, whereas irradiation generated the characteristic DMPO–O₂⁻ adduct, confirming efficient transfer of photogenerated electrons to dissolved O₂ (Figure S10). Combined with radical-quenching and control experiments, these results indicate that H₂O₂ production proceeds through a stepwise oxygen reduction pathway involving superoxide-derived surface intermediates (Figure S11).

To evaluate whether the enhanced H₂O₂ production is accompanied by improved hole utilization, the liquid-phase products of glycerol oxidation were quantified after photocatalysis (Figure S12). Both ULiNa and NaPHI generate similar major oxidation products, including glyceraldehyde, glycolic acid, dihydroxyacetone, and formic acid, indicating that Li incorporation does not alter the oxidation pathway. However, ULiNa produces larger quantities of these products than NaPHI, yielding 152 mM glyceraldehyde, 77 mM dihydroxyacetone, 32 mM glycolic acid, and 24 mM formic acid, compared with 106, 32, 30, and 18 mM, respectively, for NaPHI. A larger enhancement is observed for glyceraldehyde and dihydroxyacetone, while glycolic acid and formic acid increase more modestly. Together with the enhanced oxygen reduction kinetics, these results demonstrate that ULiNa promotes more efficient utilization of both photogenerated charge carriers. Importantly, the superior photocatalytic performance of ULiNa cannot be attributed to textural properties alone. Despite exhibiting lower specific surface area than NaPHI (Figure S13; Table S5), ULiNa delivers both faster ORR kinetics and enhanced glycerol oxidation activity. These findings indicate that the improved H₂O₂ production originates from more

efficient charge utilization arising from the electronic structure during Li-directed precursor coordination, rather than from an increased density of accessible surface sites.

Chemical structure and bonding

To gain insight into the formation pathway of ULiNa, the thermal evolution of the urea:LiCl:NaCl precursor (molar ratio = 2:0.5:0.5) was examined by thermogravimetric analysis coupled with mass spectrometry (TG-MS) (Fig. 2a). A major mass-loss event is observed below 250°C, accompanied by negligible gas evolution, indicating that the precursor initially undergoes melt-phase condensation and molecular reorganization rather than extensive decomposition. More substantial gas release is observed between 350 and 450°C, corresponding to the onset of framework formation. The dominant $m/z = 44$ signal reaches a maximum near 420°C and is assigned to CO_2 evolution during the conversion of oxygen-containing intermediates into the carbon nitride network. Concurrent $m/z = 17$ and $m/z = 30$ signals, attributed to NH_3 and N-containing fragments, respectively, reveal that deamination and framework reorganization occur simultaneously during heptazine formation. These observations suggest that the coordinated urea:LiCl:NaCl precursor promotes a controlled condensation process in which reactive intermediates are retained within the condensed phase and transformed before volatilization, thereby directing framework evolution toward a highly crystalline PHI structure. The chemical structures of the resulting materials were further examined by Fourier transform infrared spectroscopy (Fig. 2b). All samples exhibit the characteristic vibrational features of PHI, including the series of C–N and C = N stretching modes within the $1200\text{--}1650\text{ cm}^{-1}$ region and the heptazine ring breathing mode at 800 cm^{-1} , confirming preservation of the PHI framework. Additional bands centered at 987 and 1100 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of NC_2 units associated with alkali-metal-stabilized PHI structures. Although all samples exhibit similar PHI vibrational signatures, ULi displays broader and less-resolved bands, indicative of reduced structural order. On the other hand, ULiNa shows sharper features closely resembling those of NaPHI, consistent with improved framework organization. The cyano-group vibration at 2185 cm^{-1} remains comparable across all materials, excluding significant differences in terminal $\text{--C}\equiv\text{N}$ content. The local carbon environments were further probed by solid-state ^{13}C cross-polarization nuclear magnetic resonance spectroscopy (Fig. 2c). All samples exhibit two characteristic resonances centered at 156.8 and 166.2 ppm, assigned to carbon atoms within the $\text{N}=\text{C}\text{--}\text{N}_2$ (CN_3) units of the heptazine core and the sp^2 -hybridized $\text{N}=\text{C}\text{--}\text{N}(\text{H})$ species, respectively. The spectra are nearly superimposable, with no appreciable peak shifts or changes in relative intensity. These observations confirm that the simultaneous incorporation of Li and Na preserves the heptazine framework and that the enhanced performance of ULiNa does not arise from changes in the primary chemical structure, but rather from more subtle modifications introduced during framework evolution.

High-resolution transmission electron microscopy (HR-TEM) was employed to examine the crystallinity of the synthesized materials (Fig. 2d–g, Figure S14–16). All samples exhibit the lattice fringes of PHI, demonstrating that the underlying crystalline framework is maintained irrespective of the synthesis

route. NaPHI shows large, well-defined crystalline domains with clear periodicities corresponding to both in-plane and interlayer ordering (Fig. 2d). In contrast, ULi consists of smaller and less continuous crystalline regions, indicative of reduced long-range structural coherence (Fig. 2e). Upon incorporation of Na during synthesis, ULiNa exhibits larger and more ordered crystalline domains than ULi, suggesting improved framework organization (Fig. 2f and 2g). Lattice spacings of 1.03 and 0.90 nm are resolved and can be indexed to the (100) and (110) reflections of the PHI network, respectively. The corresponding fast Fourier transform (FFT) pattern displays well-defined diffraction spots characteristic of ordered in-plane periodicity observed for highly crystalline PHIs prepared from N-rich precursors and molten-salt systems.^{26,27,28,29,30,31} Powder X-ray diffraction analysis reveals that ULiNa adopts diffraction positions and relative intensities closely matching those of NaPHI (Fig. 1b). The retention of both the in-plane ordering and interlayer stacking reflections confirms that simultaneous incorporation of Li and Na preserves the underlying PHI crystal framework. In contrast, ULi presents systematic shifts of the (110) and (002) reflections toward higher diffraction angles together with broader peak profiles, consistent with lattice contraction and reduced structural coherence. These suggest that Li incorporation alone introduces greater framework distortion, whereas the presence of Na facilitates the formation of a more ordered PHI lattice. Elemental analysis further shows that the C/N ratios of ULi and ULiNa remain comparable to that of NaPHI (Table S1), confirming that all materials originate from chemically equivalent heptazine-based frameworks rather than distinct carbon nitride phases.

High-resolution X-ray photoelectron spectroscopy (XPS) was performed to probe the electronic environments of the framework atoms and incorporated alkali ions. The C 1s spectra can be deconvoluted into components at 284.8, 286.3, and 288.1 eV, assigned to adventitious carbon (C–C), cyano-related carbon species, and the sp²-hybridized carbon atoms in N–C = N units, respectively (Fig. 2h). Although the overall spectral profiles remain essentially unchanged, the N–C = N contribution in both ULi and ULiNa is shifted toward higher binding energy relative to NaPHI, indicating reduced electronic density around the conjugated framework. The cyano-related component remains identical among the three materials, in agreement with the FTIR results and excluding substantial differences in –C ≡ N content. The N 1s spectra consist of three components centered at 398.6, 400.1, and 401.0 eV, corresponding to C–N = C species, bridging/imide nitrogen (N–(C)₃), and cyano-related N, respectively (Fig. 2i). Similar positive shifts are observed for the framework N species in ULi and ULiNa, while the relative peak distributions remain unchanged. The Li 1s signal at 55 eV is detected in ULi and ULiNa, confirming successful Li incorporation (Fig. 2j). Meanwhile, the Na 1s signal in ULiNa is shifted slightly toward higher binding energy relative to NaPHI (Figure S17). The systematic positive shifts observed across the C 1s, N 1s, and Na 1s spectra consistently indicate enhanced framework polarization induced by Li-directed precursor coordination.

To further elucidate the electronic structure of ULiNa, soft X-ray absorption spectroscopy (XAS) was performed at the C and N K-edges and compared with NaPHI. The C K-edge spectra are dominated by two principal resonances at 285.3 eV (C1) and 288.0 eV (C2), corresponding to π* transitions associated with conjugated C = C/C–N states and the sp²-hybridized N = C–N moieties of the heptazine framework,

respectively (Fig. 3a). Both materials display matching spectral fingerprints, confirming preservation of the PHI backbone. Relative to NaPHI, ULiNa shows an intensified C2 resonance accompanied by increased spectral intensity in the 289–293 eV region, suggesting electronic perturbations within an otherwise structurally similar PHI framework. Similar trends are observed at the N K-edge. The N K-edge spectra are characterized by two prominent π^* resonances at 399.0 eV (N_1) and 402.5 eV (N_2), corresponding to aromatic C–N = C N atoms and bridging/imide N–(C)₃ species, respectively (Fig. 3b). While the positions of these resonances remain unchanged, ULiNa unveils enhanced intensity throughout the σ^* region above 405 eV. Taken together, the XPS and XAS measurements reveal that Li-directed precursor coordination modifies the electronic structure of PHI while preserving its chemical framework, providing direct evidence that the enhanced photocatalytic performance originates from electronically rather than structurally distinct active sites.

The nature of Li incorporation was further examined through cation-exchange experiments. Treatment of ULiNa with either Na⁺ or H⁺ solutions resulted in near-complete removal of Li, reducing its content from 1.2 wt% in the parent material to about 0.1 wt. % in both exchanged samples (Table S6). Na exchange increased the Na content from 5.3 wt% to 8.2 wt%, whereas proton exchange removed nearly all alkali ions from the framework. These results confirm that Li exists as exchangeable cations associated with the PHI structure rather than residual Li-containing phases. Although the PHI framework remained intact after ion exchange, both Na-exchanged and H-exchanged ULiNa displayed lower H₂O₂ evolution rates than the parent material and even lower than NaPHI (Fig. 3c). This trend indicates that the exceptional photocatalytic performance of ULiNa cannot be attributed solely to alkali-metal content. Instead, they indicate that the electronic structure established during Li-directed precursor coordination is irreversible and cannot be recreated through post-synthetic ion exchange.

Photo(electro)Chemical Characterizations and Catalytic Mechanism

The optical and electronic properties of the catalysts were subsequently examined. Diffuse-reflectance UV-vis spectroscopy shows that ULi and ULiNa possess slightly narrower optical bandgaps (2.66 eV) than NaPHI (2.72 eV) (Fig. 3d). While ULi exhibits an extended visible-light absorption tail characteristic of enhanced $n \rightarrow \pi^*$ transitions, the absorption profile of ULiNa closely resembles that of NaPHI despite its reduced bandgap. Valence-band XPS combined with optical bandgap analysis reveals that both the conduction- and valence-band edges of ULi shift toward more positive potentials relative to NaPHI, whereas incorporation of Na partially restores the conduction-band position, giving rise to the distinct band structure of ULiNa (Fig. 3e; Figure S18). Photogenerated charge-carrier dynamics were investigated by photoluminescence (PL), photocurrent, and electrochemical impedance spectroscopy. Compared with NaPHI, both cocrystal-derived materials exhibit quenched PL intensities, with ULiNa displaying the weakest emission, indicating suppressed radiative recombination and more efficient charge separation (Figure S19). Consistent with this trend, ULiNa generates the highest photocurrent response (Fig. 3f), demonstrating a greater population of photogenerated carriers that can be extracted and utilized in interfacial redox reactions. This behavior mirrors the enhanced electron accumulation previously observed in Li-containing ionic carbon nitrides by photoinduced absorption spectroscopy, suggesting

that Li-directed precursor coordination promotes the generation of long-lived reactive charge carriers. Electrochemical impedance spectroscopy further reveals the smallest Nyquist semicircle diameter for ULiNa (Figure S20), indicating reduced interfacial charge-transfer resistance and more efficient carrier transport. Time-resolved PL measurements (Figure S21) show prolonged average carrier lifetimes for the Li-containing materials ($\tau_{\text{avg}} = 1.58$ ns for ULi and 1.38 ns for ULiNa) relative to NaPHI ($\tau_{\text{avg}} = 1.23$ ns), confirming suppression of early-time recombination. Despite exhibiting a slightly shorter carrier lifetime than ULi, ULiNa delivers higher photocatalytic activity and photocurrent response. This observation suggests that efficient charge extraction and accumulation, rather than carrier lifetime alone, govern photocatalytic performance.

Electronic Structure Evolution and Oxygen Reduction Mechanism

To further understand the electronic origin of the superior photocatalytic performance of ULiNa, density functional theory (DFT) calculations were performed using structural models derived from the experimentally determined alkali-metal composition (1.2 wt% Li and 5.3 wt% Na). Two Na/Li configurations (3:3 and 4:2 within the PHI unit cell) were considered, with geometry optimization identifying the 4:2 arrangement as the energetically preferred structure. This configuration was therefore adopted for all subsequent calculations. The optimized structure retains the characteristic PHI framework and exhibits only minor structural distortion relative to NaPHI (Fig. 4a and 4b), indicating that Li-directed precursor coordination gives rise to an electronically distinct yet structurally conserved PHI framework. Electrostatic potential (ESP) maps reveal a redistribution of electron density across the PHI framework (Fig. 4c and 4d; Figure S22). Relative to NaPHI, ULiNa exhibits a more heterogeneous potential landscape, indicative of increased framework polarization. This redistribution mirrors the electronic perturbations observed by XPS and XAS, suggesting that Li reshapes the local electronic environment surrounding potential oxygen adsorption sites. The projected density of states (PDOS) provides further insight into how Li modifies the electronic structure of the PHI framework (Fig. 4e and 4f; Figure S23). Both NaPHI and ULiNa present a localized mid-gap state arising predominantly from the terminal $-\text{C} \equiv \text{N}$ groups, indicating that Li insertion leaves these defect-related states unaffected. More pronounced differences emerge near the valence-band edge, where ULiNa exhibits a distinct contribution from Li-derived states, whereas Na contributes negligibly. These results reveal direct electronic coupling between Li and the conjugated PHI framework, indicating that Li contributes to the frontier electronic structure rather than acting solely as a charge-compensating ion. Together, these analyses establish that Li alters the frontier electronic structure without disrupting the PHI framework.

Frontier orbital distributions further illustrate this electronic modulation (Fig. 4e and 4f; Figure S24). Whereas the highest occupied molecular orbital (HOMO) remains localized around the $-\text{C} \equiv \text{N}$ moieties, the lowest unoccupied molecular orbital (LUMO) of ULiNa extends over a larger region of the conjugated PHI network than in NaPHI. The increased LUMO delocalization reflects enhanced electronic connectivity within the conjugated framework, providing a more favorable electronic structure for interfacial oxygen reduction. Hirshfeld population analysis provides a quantitative measure of the electronic redistribution associated with Li incorporation. Compared with NaPHI, ULiNa exhibits a lower

Hirshfeld charge at the alkali-metal sites (2.1659 for the combined Na/Li sites vs. 2.688 for Na in NaPHI), indicating stronger electronic coupling between the incorporated cations and the PHI framework. A corresponding change is observed for the $-C \equiv N$ groups, whose Hirshfeld charge shifts from -0.00217 in NaPHI to 0.000699 in ULiNa. These quantitative charge redistributions confirm that Li modifies the electronic structure of the PHI framework through strong electronic coupling with the conjugated network.

The catalytic implications of the coordination-induced electronic structure were next examined through oxygen adsorption calculations. Molecular oxygen adsorbs more strongly on ULiNa, with an adsorption energy of -2.03 eV compared with -1.50 eV for NaPHI, indicating a higher affinity toward oxygen. Charge-density difference analysis reveals strong electron redistribution at the catalyst-adsorbate interface (Fig. 4h), with electron accumulation localized on the adsorbed O_2 molecule and corresponding electron depletion within the adjacent PHI framework. Hirshfeld analysis further identifies net electron transfer from ULiNa to the adsorbed O_2 molecule (-0.000144 e), demonstrating stronger catalyst-adsorbate electronic coupling. To unravel how this strengthened catalyst-adsorbate interaction influences the ORR, Gibbs free-energy profiles were calculated for the $2e^-$ ORR on NaPHI and ULiNa (Fig. 4g). The reaction proceeds through the sequential formation of adsorbed $*O_2$ and $*OOH$ intermediates before H_2O_2 formation. In comparison to NaPHI, ULiNa exhibits a consistently lower Gibbs free-energy profile throughout the entire reaction pathway. In particular, both O_2 adsorption ($*O_2$) and formation of the key $*OOH$ intermediate are significantly stabilized on ULiNa, lowering the energetic requirements for oxygen reduction. As $*OOH$ is the pivotal intermediate governing the selective $2e^-$ ORR pathway, its stabilization provides a thermodynamic explanation for the experimentally observed enhancement in H_2O_2 production. The $*H_2O_2$ intermediate is likewise thermodynamically stabilized, indicating favorable product formation without introducing additional energetic penalties. Collectively, these calculations demonstrate that the electronic structure established through Li-directed precursor coordination strengthens O_2 adsorption and stabilizes the reaction intermediates along the $2e^-$ ORR pathway, providing a molecular-level explanation for the exceptional photocatalytic H_2O_2 production of ULiNa.

3. Conclusion

In summary, we have demonstrated that coordination-defined ICCs offer a powerful platform for engineering the electronic structure of ionic carbon nitrides. Unlike conventional ionothermal synthesis or post-synthetic ion exchange, preorganized Li-carbonyl coordination within a crystalline ICC directs framework evolution during polymerization, leading to modified electronic states that promote oxygen activation, efficient charge utilization, and selective $2e^-$ ORR. The resulting PHI photocatalyst achieved an apparent quantum yield of 89% at 410 nm for photocatalytic H_2O_2 synthesis while requiring lower salt consumption than conventional ionothermal approaches. More importantly, this work establishes precursor coordination chemistry as a synthetic design principle for tailoring the electronic properties of polymeric semiconductors without fundamentally altering their chemical framework. We anticipate that

coordination-defined ICCs will provide a versatile foundation for developing next-generation ionic carbon nitrides and other organic semiconductors for solar energy conversion and photocatalytic chemical synthesis.

4. Methods

4.1 Catalyst preparation

Synthesis of NaPHI

Sodium poly(heptazine imide) (NaPHI) was synthesized following the methodology outlined in a previous publication.¹ Melamine (1 g) was grinded for 5 min at 25 Hz, using a steel ball mill vessel, with NaCl (10 g). The reaction mixture was then transferred into a porcelain crucible which was covered with a lid, placed in a heating oven and heated under a constant nitrogen flow (5 L min^{-1}) to 600°C with a heating rate of 2.3°C/min , held at 600°C for 4 hours, then allowed to cool down. The actual temperature inside the oven chamber could vary by up to 50°C . The resulting melt was removed from the crucible and transferred to a 250 mL Erlenmeyer flask with 250 mL of deionized H_2O and was stirred at room temperature overnight. Then the product was washed with approximately 1 L of deionized H_2O through a vacuum filtration system, isolated by centrifugation (13500 min^{-1} , 10 min) and dried in a vacuum oven at 60°C overnight.

Synthesis of ULi(x:y): ULi was synthesized following the same procedure as NaPHI but in this case Urea was grinded, using a steel ball mill container, with LiCl in different molar ratios ($x:y = 1:3, 1:2, 1:1, 2:1, 3:1, 4:1$).

Synthesis of ULiNa(x:y): ULiNa was synthesized following the same procedure as ULi(x:y) but in this case instead of only LiCl a salt mixture of LiCl/NaCl was used. Urea was grinded, using a steel ball mill vessel, with LiCl and NaCl in different molar ratios, where y is the sum of the two salts ratio ($x:y = 1:2, 1:1, 2:1, 3:1$).

Synthesis of UPHI

UPHI was synthesized according to a previously reported publication.² 2.5 g of Urea and 12.5 g of NaCl/LiCl eutectic mixture (0.55/0.45 ratio) were placed in a steel ball mill container and grinded for 5 minutes at 25 Hz. The mixture was then placed into a porcelain crucible covered with a lid and placed in a furnace where the temperature was increased, under a flow of N_2 gas (5 L min^{-1}), to 600°C within 4 h (rate 138°C h^{-1}) and then maintained for other 4 h. afterward, the furnace was let to spontaneously cool down to room temperature. The product from the crucible was then transferred to a 250 mL Erlenmeyer flask with 250 mL of deionized H_2O and was stirred at room temperature overnight. Then the product was washed with approximately 1 L of deionized H_2O through a vacuum filtration system, isolated by centrifugation (13500 min^{-1} , 10 min) and dried in a vacuum oven at 60°C overnight.

Synthesis of U2S

The synthesis of U₂S follows a two-step protocol previously reported in the literature.³ Urea (10 g) was heated in a furnace to 600°C for 4 h at a rate of 2.3°C min⁻¹ and then the temperature was maintained for other 4 h. After that, 900 mg of the preheated sample was ground, using a steel ball mill vessel, with 4.5 g of NaCl/LiCl eutectic mixture (0.55/0.45 ratio). Then the mixture was heated in the same conditions as the Urea precursor. After the furnace was allowed to naturally cool down to room temperature, the same washing and drying procedure used for UPHI was followed.

Synthesis of LiNaPHI (1, 5 and 10 min)

LiNaPHI was synthesized according to a study reported in a previous publication.⁴ Ion exchange was done by adding NaPHI (0.2 g) in a 1M LiCl solution (20 mL of deionized H₂O). By adding dropwise 0.1 M LiOH solution the pH value was adjusted to 9–10. The suspension was then stirred for different times (1, 5 and 10 min) at room temperature and washed several times through centrifugation (5 x 2mL, 13500 min⁻¹, 10 min). The resulting powder was obtained after drying in the vacuum oven at 60°C overnight.

4.2 General Characterizations

X-ray powder diffraction (XRD) was performed using a Rigaku Smart Lab (Japan, Cu K, 0.154 nm) at a generator voltage of 40 kV and a current of 50 mA, with a scanning speed of 1° /min from 5° to 60°. The chemical composition and chemical states were obtained with an Axis Supra+ (Kratos Analytical, UK) X-ray photoelectron spectroscopy (XPS) setup using monochromatised Al K α / Ag L α radiation for excitation (15 kV, 20 mA). CasaXPS software was used for data processing and interpretation. Fourier Transform Infrared (FTIR) spectroscopy measurements were carried out using a Thermo Scientific Nicolet iD5 spectrometer with an attenuated total reflection sampling technique. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted using a PerkinElmer ICP-OES Optima 8000. Elemental combustion analysis (EA) was performed with an EA3100 Elemental Analyzer (EuroVector Srl, Pavia, Italy) in two different modes (combustive for carbon, hydrogen and nitrogen; non-combustive for oxygen). The isotherms obtained from N₂ physisorption were analyzed using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method to calculate total specific surface area and pore size distribution; the data were measured at 77 K with a Quantachrome Quadrasorb SI instrument. Ahead of each measurement, the samples were degassed at 150 °C under vacuum (0.5 Torr) for 15 hours and the specific surface area of each material was calculated from the adsorption branch data, in the pressure range from 0.05 to 0.3, using the BET method.⁵ Transmission electron microscopy (TEM) images were taken using JEOL JEM F200 and a double Cs corrected JEOL JEM-ARM200F operated at 80kV and equipped with a cold-field emission gun and high-angle silicon drift Energy Dispersive X-ray (EDX) detector (Jeol JED-2300 100 mm², Japan)(solid angle up to 0.98 steradians with a detection area of 100 mm²). UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was performed using a Shimadzu UV 2600. Electron paramagnetic resonance (EPR) results were acquired

using a Bruker EMXnano. Steady-state photoluminescence (PL) spectra were measured with a Jasco FP-8300 fluorescence spectrometer at an excitation wavelength of 365 nm and time-resolved PL (TRPL) spectra were recorded on fluorescence lifetime spectrometer (FluoTime 250, PicoQuant) equipped with PDL 800-D picosecond pulsed diode laser drive. The average lifetime (τ_{avg}) is calculated as follows:

$$\tau_{\text{avg}} = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2)}{(A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3)} \quad (1)$$

4.3 Photocatalytic Experiments

4.3.1 Photocatalytic H₂O₂ Production

Photocatalytic H₂O₂ production experiments were conducted in a 4 mL vial reactor were, initially, 5 mg of the catalyst was dispersed in 2 mL of a 10%w/w glycerin aqueous solution then O₂ gas was bubbled through the mixture for 1 min. The solution was next irradiated, while continuously stirring, using two purple LED (50 W each, $\lambda = 410$ nm), placed at a distance of 12 cm each from the reactor, for 1 h. The resulting suspension was then centrifuged at 13300 rpm for 10 min to separate the catalyst from the solution. The amount of H₂O₂ generated was quantified spectrophotometrically following the titanium oxalate method.⁶ Principally, a 10 g L⁻¹ solution of K₂[TiO(C₂O₄)₂]•2H₂O was prepared using 450 mL of water and 50 mL of sulfuric acid to avoid the complex precipitation. Then, 1.5 mL of this complex was mixed with 0.5 mL of the supernatant from the photocatalytic reaction. The prepared solutions were analyzed with a UV-vis spectrometer, after appropriate dilution when necessary, measuring absorbance at 400 nm. To ensure accuracy, a calibration curve was constructed using external samples with known H₂O₂ concentrations ranging from 0 to 10 mmol L⁻¹, yielding a highly linear analytical response ($R^2 = 0.99996$).

4.3.2 Apparent Quantum Yield (AQY) Estimation

The AQY was measured using different monochromatic lights (365, 410, 465 and 525 nm). The AQY value was obtained through the following equation:

$$\text{AQY (\%)} = \frac{2 \times r_{\text{product}} \times N_A \times hc}{I \times A \times \lambda} \times 100 \quad (2)$$

where r_{product} is the production rate of H₂O₂ molecules (mol s⁻¹) after the first hour of photocatalytic reaction, N_A is the Avogadro number (6.022×10^{23} mol⁻¹), h is the Planck constant (6.626×10^{-34} J s⁻¹) multiplied by c that is the speed of light (3×10^8 m s⁻¹) giving ($1.98644586 \times 10^{-25}$ J m), A is the irradiation area (cm²), I is the intensity of the irradiation light (W cm⁻²), and λ is the wavelength of the monochromatic

4.3.3 Radical Quenching experiments

In a 4 mL reaction vial, 5 mg of the ULiNa powder was dispersed in 2 mL of a 10%w/w glycerin aqueous solution along with a 10 mM sacrificial reagent: AgNO₃ for e⁻, Na₂SO₃ for •O₂⁻ and t-butyl alcohol (TBA)

for $\bullet\text{OH}$. Then, O_2 gas was bubbled through the mixture for 1 min. The solution was irradiated, while continuously stirring, using two purple LED (50 W each, $\lambda = 410 \text{ nm}$), placed at a distance of 12 cm each from the reactor, for 1 h. The amount of H_2O_2 generated was quantified spectrophotometrically following the titanium oxalate method.⁶

4.3.4 Electron Paramagnetic Resonance (EPR) experiment

The presence of $\bullet\text{O}_2^-$ in the reaction system has been proven using EPR where 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was employed as the spin-trapping agent to detect radicals. The sample for the measurements was prepared by adding, initially, 400 μL of H_2O to 1 mg of the catalyst, followed by sonication for 10 minutes. Immediately before the measurements 0.1 mmol of DMPO and 100 μL of methanol were added to the solution. The measurements were conducted twice for each sample: first in the dark, and then after 10 minutes of irradiation with a 410 nm LED as the light source.

light (m).

4.4 Photo(Electro)chemical Measurements

The photo(electro)chemical measurements were performed in a three-electrode configuration, using Ag/AgCl and a Pt wire as reference and counter electrodes, respectively. The experiments were carried out with a Gamry Interface 101E Potentiostat. The working electrode was prepared using a F-doped Tin Oxide (FTO) glass (3 x 1 cm) previously cleaned with detergent, distilled water and sonicated for 15 min in ethanol to remove organic impurities. The catalyst ink was obtained by sonication for 30 min of 5 mg of the catalyst in 0.5 mL of H_2O and 20 μL of a 5 wt.% Nafion solution. Next, 50 μL of the ink was pipetted onto a 1 x 1 cm surface of the FTO electrode, dried on a heating plate at 70°C and, after it is completely dry, the temperature was increased to 120°C for 1 h to improve adhesion. All the measured potentials were converted to reversible hydrogen electrode (RHE) according to the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \cdot \text{pH} \quad (3)$$

All the experiments were tested with a 0.2 M Na_2SO_4 electrolyte solution (pH = 7, O_2 -saturated).

4.4.1 Electrocatalytic Oxygen Reduction reaction (ORR)

Rotating ring-disk electrode (RRDE) or rotating disk electrode (RDE) technique was used to measure the number of transferred electrons (n) of the samples during the ORR. The measurements were also investigated using the standard three-electrode system. Similarly, the Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. To prepare the catalyst ink, 6 mg of the catalyst and 6 mg of black carbon were fully ground and disperse in pure water (490 μL), isopropanol (490 μL) and Nafion solution (20 μL) via sonication for 1 h. After this, 10 μL of ink was dropped onto a clean glassy carbon electrode and dried at room temperature for 1 h. Different rotating speeds were used for the RRDE (300, 600, 900, 1200, 1600) and the potential range was set to 0–1.0 V vs RHE. The linear sweep voltammetry (LSV) is performed on the disk electrode, while a constant potential (e.g. 1.2 V vs. RHE) is applied on the

ring electrode. When H_2O_2 is produced on the disk, it can diffuse to the ring then be detected and the number of transferred electrons (n) was calculated according to the slopes of the Koutecký-Levich plots with the following equation:

$$B = 0.2nFC_0D_0^{2/3} \nu^{-1/6} \quad (4)$$

Here, F is the Faraday constant (96485 C/mol), C_0 is the bulk concentration of O_2 (1.1×10^{-3} mol/cm³), D_0 is the diffusion coefficient of O_2 (1.1×10^{-5} cm²/s) and ν is the dynamic viscosity of H_2O (0.01 cm²/s).

4.4.2 Transient photocurrent response (TPC)

The photocurrent response was measured at 0.3 V versus reference electrode in 0.2 M aqueous Na_2SO_4 solution under purple LED ($\lambda = 410$ nm) illumination using a Gamry Interface 1010E potentiostat.

4.4. 3 Electrochemical impedance spectroscopy (EIS)

For EIS, the measurements were performed, after immersing the electrodes in a 0.2 M aqueous Na_2SO_4 solution, in a frequency range of 10 kHz to 1 Hz. The data were fitted using Z-View software to obtain a full semicircle.

4.4.2 Mott-Schottky measurements (MS)

MS measurements were conducted in a Biologic MPG-2 system at 10 KHz using the same electrodes as described above.

5. Computational method

Density functional theory (DFT) calculations were performed to investigate the structural stability, electronic structure, and oxygen reduction reaction (ORR) energetics of the PHI catalysts. Geometry optimization, electrostatic potential (ESP), frontier molecular orbital, adsorption-energy, Gibbs free-energy, Hirshfeld population, and charge-density difference analyses were carried out using the **ORCA 6.1.0** package⁷ with the **r²SCAN-3c** composite functional.⁸ This composite method combines the meta-generalized gradient approximation (meta-GGA) exchange-correlation functional with dispersion, basis-set, and basis-superposition corrections, providing reliable geometries and energetics at moderate computational cost.

Charge-density difference (CDD) was calculated to evaluate the interfacial charge redistribution during O_2 adsorption according to

where, ρ_{ULiNa} and ρ_{O_2} denote the electron densities of the adsorption complex, the isolated catalyst, and the isolated O_2 molecule, respectively. Positive and negative values of $\Delta\rho$ correspond to electron accumulation and electron depletion upon adsorption, respectively.

The adsorption energy of oxygen reduction intermediates was calculated according to

$$\Delta E_{\text{ads}} = E(*\text{adsorbate}) - E(*) - E(\text{adsorbate})$$

where $E(*\text{adsorbate})$, $E(*)$, and $E(\text{adsorbate})$ represent the total energies of the adsorbate-bound catalyst, the pristine catalyst, and the isolated adsorbate (O_2 , $*\text{OOH}$, or H_2O_2), respectively. A more negative adsorption energy indicates a stronger interaction between the adsorbate and the catalyst surface.

The Gibbs free energy of each elementary ORR step was obtained from

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S,$$

$$\Delta G_1 = G(\text{O}_2*) - G(*) - G(\text{O}_2)$$

$$\Delta G_2 = G(\text{OOH}*) - G(\text{O}_2*) - 1/2G(\text{H}_2)$$

$$\Delta G_3 = G(\text{H}_2\text{O}_2*) - G(\text{OOH}*) - 1/2G(\text{H}_2)$$

where ΔE is the electronic energy difference, ΔE_{ZPE} is the zero-point energy correction, and $T\Delta S$ is the entropy contribution at 298.15 K.

To analyze the electronic states of the extended PHI framework, projected density of states (PDOS) calculations were additionally performed using periodic density functional theory as implemented in the Quantum ESPRESSO package.⁹ A periodic supercell model was employed to better represent the extended conjugated structure of PHI and to identify the atomic contributions to the valence- and conduction-band edges. The Perdew–Burke–Ernzerhof (PBE)¹⁰ exchange-correlation functional was adopted together with Grimme's D3 dispersion correction.¹¹ The Brillouin zone was sampled using a $2 \times 2 \times 1$ Monkhorst–Pack k -point mesh, and the structures were relaxed until the energy and force converged to 1×10^{-5} eV and $0.02 \text{ eV } \text{\AA}^{-1}$, respectively

All structural models and isosurface visualizations were generated using VESTA.¹⁰

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Figures

a Synthesis of Cocystal-derived Ionic Carbon Nitrides

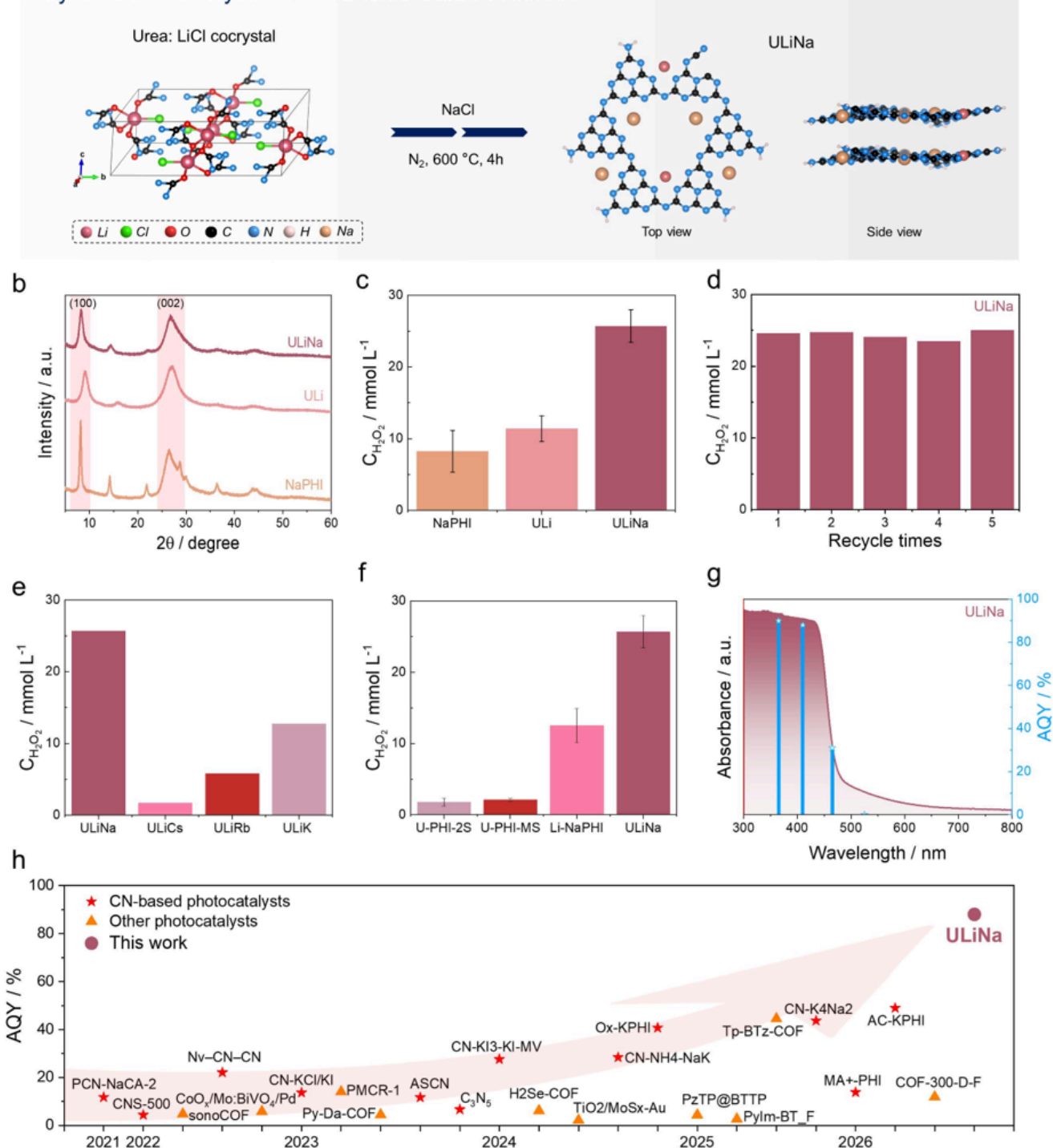


Figure 1

a) Schematic of the synthesis process for ULiNa from urea:LiCl cocrystal and NaCl (molar ratio = 2:0.5:0.5). (b) XRD patterns and (c) Photocatalytic H_2O_2 evolution activities of NaPHI, ULi (urea:LiCl molar ratio of 2:0.5), and ULiNa. (d) Recyclability tests for ULiNa in H_2O_2 production. (e) Photocatalytic H_2O_2 evolution activities of cocrystal-derived dual-cation catalysts. (f) Photocatalytic H_2O_2 production of ULiNa compared to U-PHI-MS, U-PHI-2S and Li-NaPHI. Reaction conditions for (c–f): photocatalyst, 5 mg; solvent, 2 mL of 10% w/w glycerin bubbled with O_2 for 1 min before the reaction. (g) UV-vis spectrum and AQY values for ULiNa as a function of the irradiation wavelength. (h) Comparison of the apparent quantum yields of ULiNa with representative state-of-the-art carbon nitride and non-carbon nitride photocatalysts reported in recent high-impact journals.

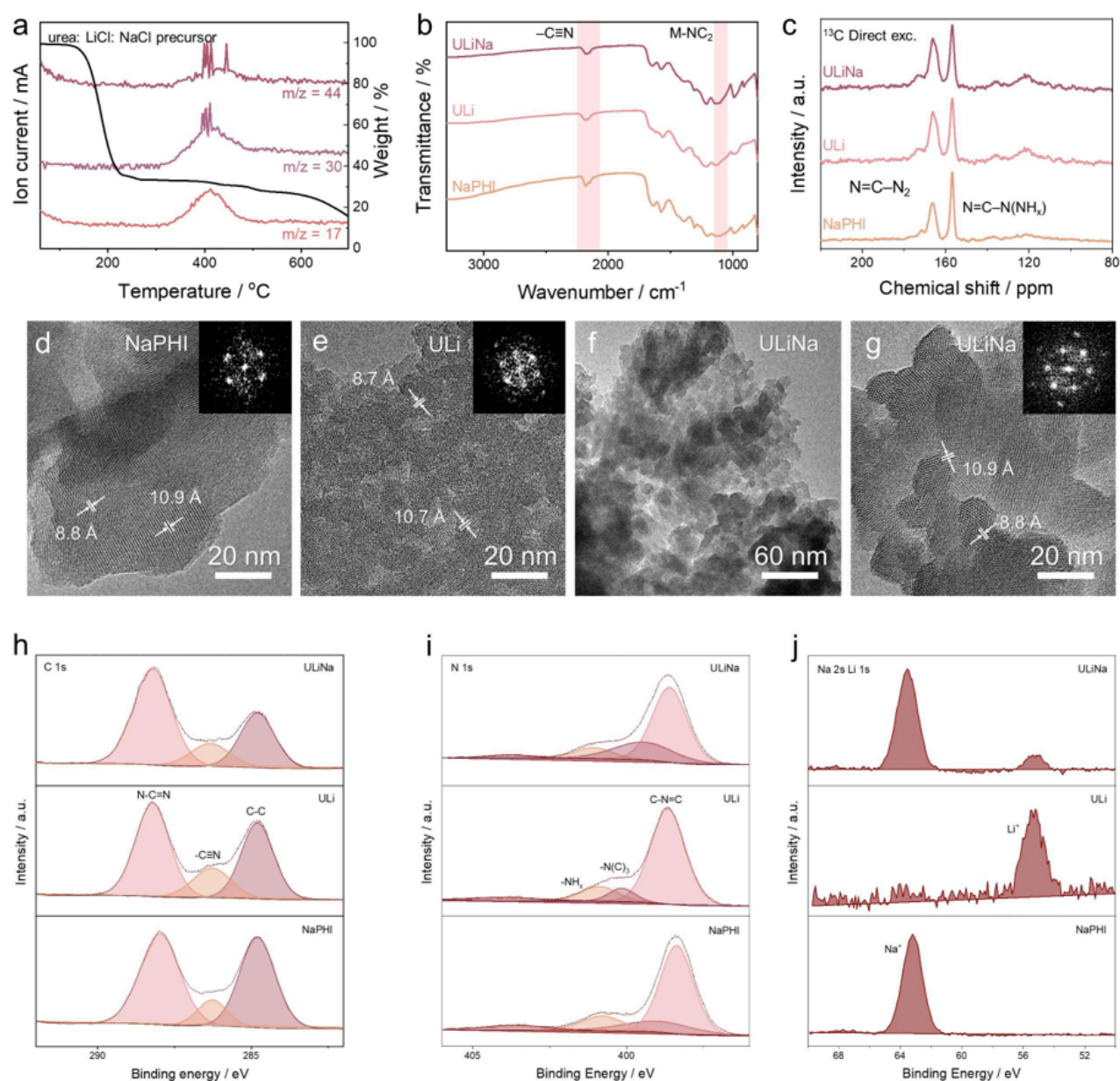


Figure 2

(a) TG-MS curve of urea:LiCl:NaCl (2:0.5:0.5 molar ratio) precursor recorded under inert atmosphere (2.5 K min^{-1}). (f) FTIR, and (g) Solid-state ^{13}C NMR spectra of NaPHI, ULi, and ULiNa. High-resolution TEM images of (d) NaPHI, (e) CALi, (f) and (g) ULiNa with their corresponding FFT images. High-resolution (h) C 1s, (i) N 1s, and (j) Na 2s and Li 1s XPS spectra of NaPHI, ULi, and ULiNa.

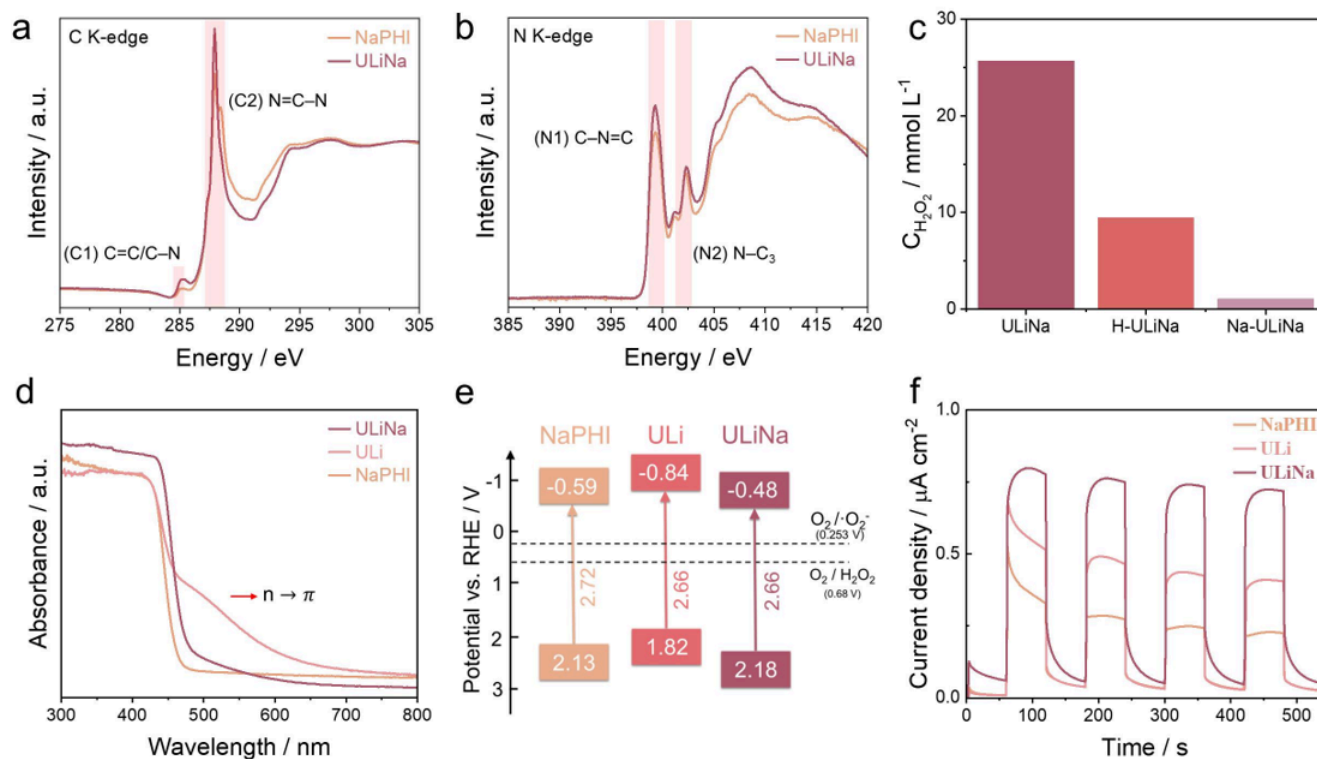


Figure 3

Normalized (a) carbon and (b) nitrogen K-edge XANES spectra of NaPHI and ULiNa. (c) Photocatalytic H₂O₂ production of pristine ULiNa compared to H- and K-exchanged counterparts. (d) Experimentally determined band structures of NaPHI, ULi, and ULiNa. (f) Transient photocurrent response (TPC, $\lambda = 410 \text{ nm}$) for NaPHI, ULi, and ULiNa in 0.2 M Na₂SO₄ aqueous electrolyte solution.

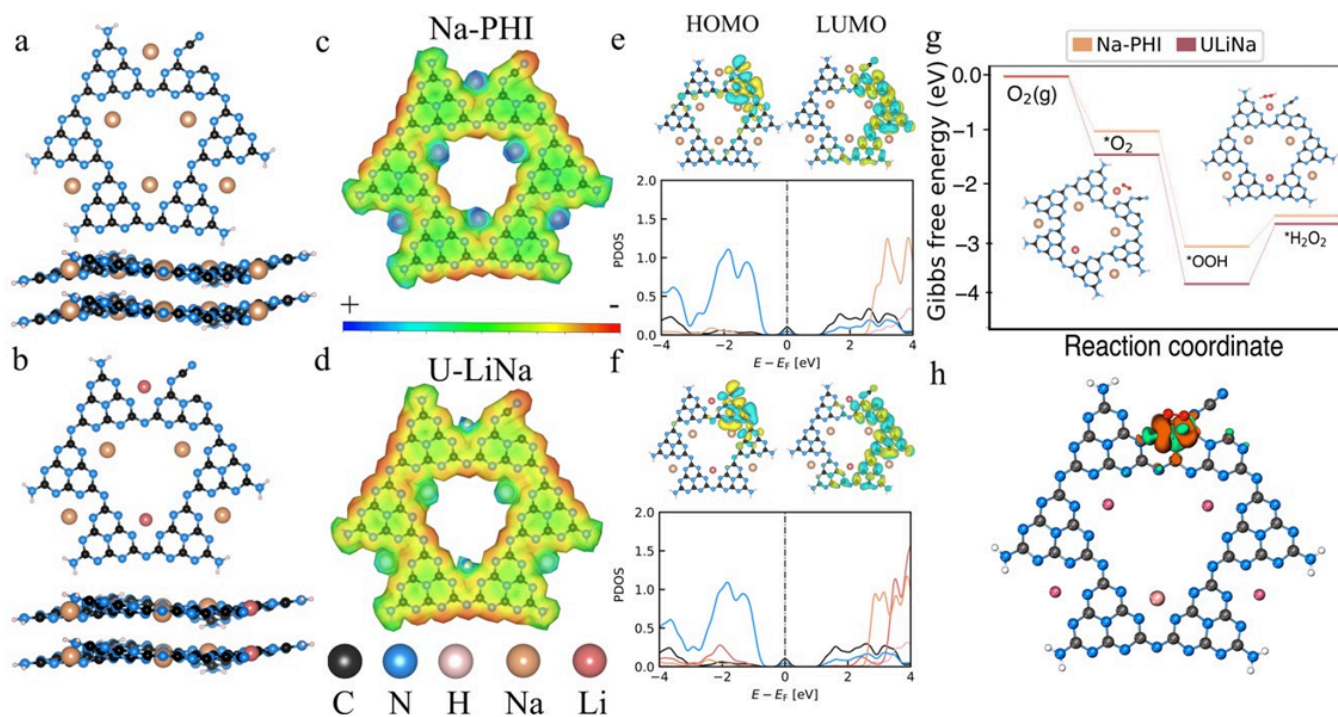


Figure 4

Top and side view of (a) Na-PHI and (b) ULiNa with their corresponding electrostatic potential maps (c,d). Regions of electron accumulation and depletion are represented by red and blue isosurfaces, respectively. HOMO, LUMO and PDOS plots of (e) Na-PHI and (f) ULiNa. (g) Gibbs free energy diagram and (h) Charge density difference of O₂ adsorption on UliNa (orange: accumulation and green depletion of charge).

Supplementary Files

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