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A Universal Framework for Ligand-Directed Artificial Photosynthesis by Hydrolyzed Titanium Complexes

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ABSTRACT

A mechanistic study of three hydrolyzed titanium–ligand complexes 2-phenylindole (PI)–$TiCl_4$, 2-phenylbenzoxazole (BZX)–$TiCl_4$, and 1,10-phenanthroline (Phen)–$TiCl_4$—reveals a unified pathway for Direct Air Capture (DAC) and photocatalytic conversion of atmospheric CO_2 under ambient conditions. The process exemplifies a radical-driven form of artificial photosynthesis powered by the intrinsic redox activity of hydrolyzed titanium species that continuously generate hydroxyl radicals (•OH), the true life-sustaining agents of the system.

To elucidate the underlying mechanism, the overall photocatalytic transformation can be resolved into three interconnected stages each governed by the evolving speciation, redox state, and ligand environment of titanium. Together, these stages trace the system's progression from spontaneous hydrolysis to radical-driven CO_2 reduction and selective product formation.

Stage 1: Spontaneous hydrolysis and partial reduction of $TiCl_4$–ligand mixtures by atmospheric moisture and oxygen produce disordered yet functionally organized ensembles of hydrolyzed and reduced Ti species. This initial structural diversity provides a self-adjusting equilibrium of coordination environments that primes the system for autonomous catalysis. Each ligand introduces a distinct molecular template that shapes the redox potential landscape and directs the ensuing transformations.

Stage 2: Progressive hydrolysis establishes equilibria between hydrated Ti species and $TiCl_2O$ units containing reduced Ti centers capable of capturing and activating atmospheric CO_2. Upon visible-light excitation, Ti–OH bonds act as radical precursors, releasing •OH radicals that concurrently regenerate reduced Ti sites and reduce carbonate intermediates to formaldehyde—the hallmark product of Reactive DAC.

Stage 3: This marks the divergence of ligand-controlled photochemistry. In the PI and BZX systems, hydroxyl-radical cascades extend formaldehyde into oxygenates reaching up to C_{17}, while in the Phen system, the same radical flux channels formaldehyde exclusively into polyoxymethylene (POM). These complementary outcomes expose the dual advantage of titanium chemistry: the ability to both generate and exploit hydroxyl radicals as reductants and molecular architects.

Collectively, the three systems define a self-sustaining, light-driven framework for artificial photosynthesis, in which hydroxyl radical dynamics, ligand templating, and environmental reactants (H_2O, O_2, CO_2) cooperate to achieve selective and extended CO_2 reduction under ambient conditions a level of autonomous photochemical integration not achieved by any other known photocatalytic system.

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Introduction

Artificial photosynthesis represents one of the most ambitious frontiers in sustainable chemistry-an effort to emulate the natural photosynthetic cycle through the autonomous conversion of CO_2 and H_2O into energy-rich organic products. Despite decades of progress, most systems remain constrained by multi-component architectures, sacrificial agents, or narrow selectivity toward short-chain products. What remains elusive is a **self-sustaining, single-matrix photocatalyst** capable of directly capturing atmospheric CO_2 and transforming it into higher organic molecules under ambient conditions.

Among transition metals, **titanium stands uniquely poised** to meet these requirements. Its high oxophilicity, variable oxidation states (Ti^{4+}/Ti^{3+}), and photoactivity create a fertile ground for redox-driven chemistry. However, traditional Ti-based photocatalysts, such as TiO_2, require bandgap excitation and external biasing, producing only limited CO_2 reduction products [1]. The essential missing link has been the recognition that **titanium hydrolysis is not a complication but the engine of its reactivity**, as hydrolyzed Ti–OH groups can serve as both radical precursors and charge relays within dynamic aqueous–organic interfaces [2,3].

This principle defines a **radical-driven paradigm for artificial photosynthesis**, in which the photoactivation of hydrolyzed organotitanium complexes generates hydroxyl radicals **(•OH)** that mediate both electron transfer and molecular assembly. In this

framework, •OH radicals are not mere oxidants but multifunctional actors that drive Ti reduction, CO_2 activation, and carbon–carbon coupling. The result is an **autonomous catalytic cycle** powered entirely by ambient light, moisture, and CO_2-a process that merges photophysics, redox chemistry, and self-organization into a single evolving matrix.

To explore this paradigm, three representatives hydrolyzed $TiCl_4$–ligand systems were investigated: **2-phenylindole (PI), 2-phenylbenzoxazole (BZX),** and **1,10-phenanthroline (Phen)** [4-7]. Each ligand modulates the Ti coordination sphere, redox balance, and radical dynamics in distinct ways, defining separate pathways for CO_2 conversion [8]. The **PI–$TiCl_4$** complex promotes hydroxyl-radical-driven condensation of formaldehyde to yield oxygenates extending to C_{17}. The **BZX–$TiCl_4$** complex follows a similar cascade, producing mid-range aldehydes (C4–C8) through aldol-type processes. In sharp contrast, the **Phen–$TiCl_4$** complex channels the same reactive intermediates toward the exclusive formation of **polyoxymethylene (POM)**—a polymeric product that mimics the carbohydrate framework of biological systems.

In all three systems, **hydroxyl radicals perform the dual function** of reconstituting reduced Ti centers and initiating selective C–C bond formation, while the Ti–ligand matrix autonomously captures and activates atmospheric CO_2. The outcome is a **self-renewing photocatalytic** environment that continuously reorganizes and adapts, reflecting a level of functional integration rarely achieved in synthetic systems.

This study establishes that **without hydroxyl radicals, Ti chemistry would remain photochemically inert**; with them, it becomes a self-sufficient engine of atmospheric CO_2 fixation and molecular synthesis. Hydroxyl radicals (.OH) are arguably the most sought-after oxidative species in photocatalysis, due to their nonselectivity and high oxidation potential (2.8 V versus NHE). The present work thus introduces a coherent and universal framework for artificial photosynthesis—one in which *Ti-based radical generation, ligand templating, and environmental self-organization* converge to achieve truly autonomous carbon transformation [9].

Results and Discussion

The interaction of $TiCl_4$ with the three nitrogen- and oxygen-bearing aromatic ligands 2-phenylindole (PI), 2-phenylbenzoxazole (BZX), and 1,10-phenanthroline (Phen)—initiates a cascade of hydrolytic and redox events upon exposure to ambient air. Within minutes, the colorless mixtures evolve into tinted solutions or gels, indicating the spontaneous formation of hydrolyzed and partially reduced titanium species. **MALDI-TOF mass spectrometry** reveals a distribution of Ti-containing fragments that correspond to progressively hydrolyzed $TiCl_x(OH)_y$ units and their ligand adducts, confirming that the system self-organizes into a population of reactive intermediates rather than a single molecular entity [10,11]. This ensemble represents the **dynamic catalytic matrix** responsible for both CO_2 capture and light-driven transformation.

UV–Vis spectroscopy further confirms the redox-active nature of these complexes. Broad charge-transfer bands extending into the visible region (350–500 nm) indicate that ligand-to-metal (π→Ti) transitions occur upon illumination, activating Ti–OH bonds as radical precursors. The **photoinduced cleavage of Ti–OH** produces hydroxyl radicals (•OH), whose redox potential (~+2.8 V vs NHE) exceeds that of the Ti^{4+}/Ti^{3+} couple (~–0.1 V), enabling the simultaneous oxidation of water and reduction of titanium centers. This cyclic regeneration of Ti^{3+} provides the reducing equivalents necessary for the **autonomous conversion of atmospheric CO_2** into formaldehyde and higher organic intermediates.

It should be noted that the use of $TiCl_4$ is critical for achieving the observed redox-active hydrolyzed complexes. Among the titanium tetrahalides, chloride provides an optimal balance of Lewis acidity, hydrolytic lability, and visible-light charge-transfer character. Replacement by fluoride would produce a more inert, non-hydrolyzing Ti–F framework, suppressing Ti–OH and Ti–O• formation and thus hindering photocatalytic CO_2 conversion. Conversely, bromide or iodide analogues, while more photoactive, would likely be unstable under ambient hydrolysis conditions. Hence, chloride uniquely enables the coupled hydrolysis and redox cycling required for autonomous CO_2 capture and conversion in the present systems.

At this stage, the role of the ligand becomes decisive. Each ligand imposes a **unique electronic and steric template** that channels the evolving Ti–OH/•OH reactivity along different photochemical trajectories. In the PI– and BZX–$TiCl_4$ systems, hydroxyl radical activity initiates the **cascade condensation of formaldehyde**, producing oxygenated products extending from C_2 to C_{17}, depending on the ligand's stabilization of intermediate alkoxide and enolate species. These transformations are consistent with aldol-type C–C coupling under radical conditions, forming extended carbon chains through successive $–CH_2–$ additions.

In contrast, the Phen–$TiCl_4$ system diverges sharply. The bidentate chelation and rigid aromatic framework of 1,10-phenanthroline stabilize Ti–O–Ti linkages that favor **polymerization of formaldehyde into polyoxymethylene (POM)** rather than condensation into higher oxygenates. The same hydroxyl-radical chemistry thus gives rise to a distinct pathway—**a light-driven mimic of carbohydrate formation**—highlighting the ligand-dependent selectivity of the radical-driven process.

Stage 1: The Disordered Onset in the Monodentate PI–$TiCl_4$ System

Among the three systems examined, the **2-phenylindole–$TiCl_4$ (PI–$TiCl_4$)** complex offers the most transparent view of the initial stage of photocatalyst formation. Upon coordination, 2-phenylindole undergoes **proton transfer to its indolenine form**, which binds $TiCl_4$ primarily through a **π-type interaction at the C=N bond**. The resulting coordination is **monodentate and relatively labile**, providing little geometric or electronic stabilization to the titanium center. Consequently, upon exposure to atmospheric moisture and oxygen, the system evolves into a **disordered yet functionally rich ensemble** of partially hydrolyzed and redox-active species rather than a single, well-defined adduct.

The composition of this early ensemble is strongly dependent on the **ligand-to-metal ratio**. At a **1:1 ratio**, incomplete coordination leaves titanium highly susceptible to hydrolysis, producing a broad distribution of Ti–OH and Ti–O–Ti species. With excess **$TiCl_4$ (1:2)**, the environment becomes highly Lewis-acidic, promoting rapid hydrolysis but destabilizing the organic component through competitive protonation and chloride exchange. Conversely, **excess ligand (2:1)** saturates the coordination sphere, suppressing hydrolysis and reducing the concentration of reactive Ti–OH sites. Empirically, a **1:1.3 $TiCl_4$:PI ratio** provides the most effective balance—sufficient coordination to sustain photochemical activity while maintaining accessibility for **controlled hydrolysis and redox initiation** [6].

Because the π-bonded coordination offers minimal structural templating, the evolution of the system is strongly influenced by **external parameters**—ambient humidity, oxygen content, temperature, solvent polarity, and reagent-mixing order. These factors collectively determine the rate and uniformity of **Ti–OH formation**, which constitutes the critical chemical outcome of Stage 1. Upon illumination, the Ti–OH units undergo **photoinduced homolytic cleavage**, generating **hydroxyl radicals (•OH)** while partially reducing titanium from Ti^{4+} to Ti^{3+}. This self-initiated radical generation marks the true onset of catalytic life in the system and sets the energetic foundation for the subsequent photocatalytic cascade.

Stage 1: Early Disordered Matrix of the 2-Phenylbenzoxazole–$TiCl_4$ System

The **MALDI-TOF profile** and corresponding molecular assignments (Figure 1) reveal that the initial exposure of the 2-phenylbenzoxazole–$TiCl_4$ (BZX–$TiCl_4$) mixture to ambient atmosphere produces not a single coordination adduct but a **heterogeneous matrix of monomeric and dimeric intermediates**. Within this matrix, **partial hydrolysis, ligand exchange, and internal redox events** occur concurrently, giving rise to a broad distribution of species spanning m/z ≈ 170–855-an unmistakable signature of the "chaotic" onset characteristic of this system.

At the outset, the ligand engages $TiCl_4$ primarily through a **π-type interaction involving both heteroatoms (N and O)** rather than forming a rigid σ-chelate. This delocalized binding facilitates **rapid ligand exchange and hydrolysis**, enabling chloride displacement and the concurrent appearance of **Ti–OH and Ti–H fragments**. The detection of mixed-valent Ti(IV)/Ti(III)/Ti(II) species indicates that **internal redox equilibration** has begun, with the π-donor ligand mediating electron transfer from coordinated hydroxide or hydride units to the titanium center.

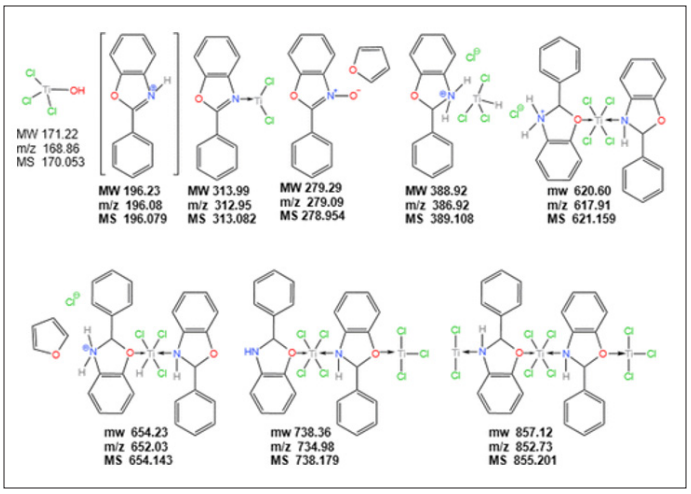

Figure 1: Stage 1 in the Evolution of the Bzx–Ticl₄ System: Spontaneous Hydrolysis and Structural Reorganization Generate a Dynamic Ensemble of Reduced and Hydrolyzed Ti Centers that Prime the Matrix for Light-Driven Co₂ Conversion

Simultaneously, **salt-like ionic species** emerge as protonated ligand cations pair with $TiCl_x(OH)_y^-$ fragments. Distinct signals assigned to **hydrated $TiCl_3OH$ units** demonstrate that water coordination and hydroxide formation occur preferentially at **partially reduced Ti sites**, rather than on the initially π-bound ones. Notably, no Ti–O–Ti linkages are detected at this stage, confirming that **oligomerization is confined to dimeric assemblies** stabilized by hydrogen bonding or weak chloride bridges, rather than condensation into extended oxo networks.

The resulting ensemble constitutes a **disordered yet redox-active matrix** in which hydrolysis, ligand protonation, and Ti reduction proceed in concert. Each molecular fragment represents a transient configuration along the evolving pathway from an initial π-bound adduct toward the **σ-bonded, photoreactive species** that dominate later stages. This early chemistry defines the **energetic groundwork for Stage 2**, establishing a reservoir of reactive Ti–OH and Ti–H sites that, upon illumination, generate hydroxyl radicals and initiate the **autonomous photoreduction of atmospheric CO_2**.

Stage 1: Early Hydrolyzed Ensemble of the phen–$TiCl_4$ System

Exposure of the phen·$TiCl_4$ complex to ambient moisture initiates a striking sequence of hydrolysis, protonation, and redox processes that define the earliest stage of catalyst maturation. Trace water and oxygen activate Ti–Cl bonds, producing a dynamic mixture of Ti–OH, Ti=O, and Ti–oxo species. Within this evolving medium, the protonated form of phenanthroline (phenH)+ rapidly emerges as a key organizing component. Acting simultaneously as proton donor, counterion, and supramolecular stabilizer, $phenH^+$ orchestrates the pace of Ti–Cl hydrolysis, suppresses uncontrolled precipitation, and promotes the progressive formation of hydroxylated and partially reduced Ti centers [12].

Through hydrogen bonding and electrostatic pairing with anionic Ti–oxo intermediates, $phenH^+$ imparts charge balance and colloidal stability, converting an initially amorphous mixture into a coherent, redox-active network. The onset of mixed-valent Ti^{3+}/Ti^{4+} domains and emerging intervalence charge-transfer (IVCT) features signal the development of electronic communication across this nascent matrix.

The MALDI–TOF spectrum interpretation (Figure 2) captures this transformation vividly, displaying a continuum of species from low-mass Ti chlorohydroxo fragments to extended hydroxyl-rich oligomers (assigned structures 3–16). Persistent $phenH^+$ signals, both as free ions (structure 1) and coordinated chelates (structure 2), confirm that ligand protonation accompanies early hydrolysis. Phen thus operates as a bidentate template that stabilizes discrete phenH·Ti motifs and directs hydrolysis toward $TiCl_x(OH)_y$ fragments instead of uncontrolled oxo condensation.

Lower-mass ions (3–7) trace successive Ti–Cl → Ti–OH substitution steps, while higher-mass features (8–16) reveal linear hydroxide-bridged oligomers in which Ti remains coordinated to $phenH^+$ or neutral phen chelates. The frequent appearance of HCl adducts and hydrated $TiCl_3OH$ units further attests to a coupled sequence of proton transfer, chloride displacement, and controlled hydrolysis.

Collectively, this early-stage chemistry defines a self-organized, hydroxyl-rich reservoir of reactive Ti centers—a redox-active ensemble preconfigured by $phenH^+$ for subsequent photoinduced hydroxyl radical generation, CO_2 activation, and POM formation in the photochemical stage.

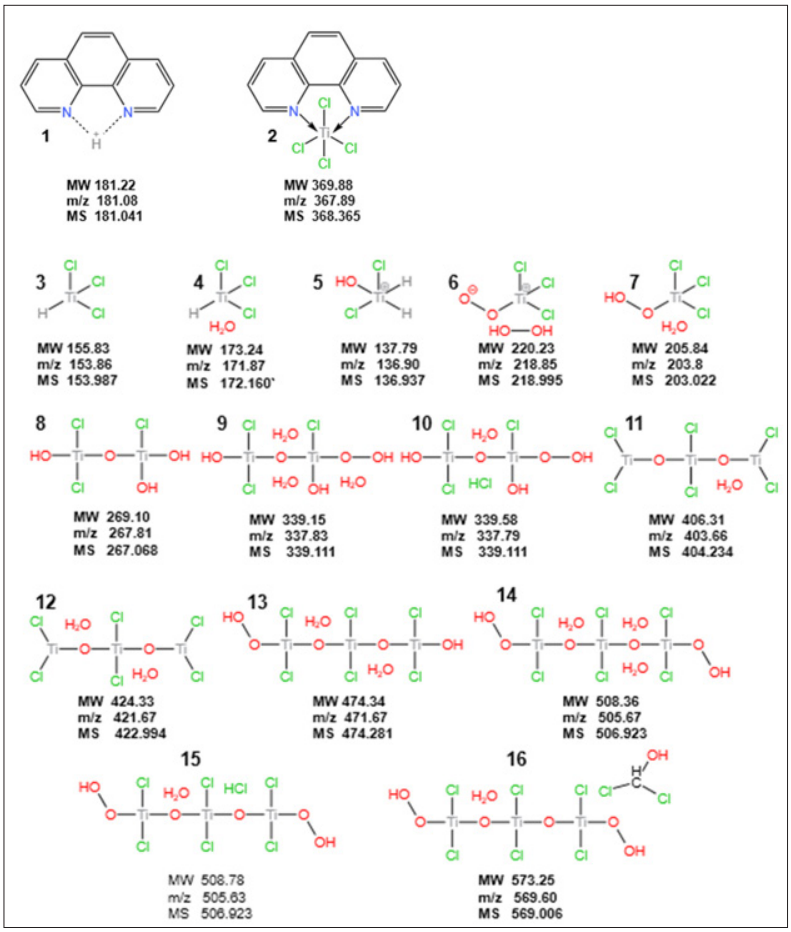

Figure 2: Early-Stage Evolution of the Phen–$TiCl_4$ System: Hydrolysis and Redox self-Adjustment Generate a Disordered yet Functionally Organized Matrix of Hydrolyzed Ti Species that Seed Autonomous Photocatalytic Behavior

Stage 2: Universal Hydrolytic–Redox Pathway and CO_2-to-Formaldehyde Conversion

The second, photochemically responsive stage of the catalytic process (Figure 3) represents the universal pathway shared by all ligand systems examined—phenanthroline (phen), 2-phenylindole (PI), and 2-phenylbenzoxazole (BZX)—and, by extension, by any aromatic ligand capable of coordinating to titanium and engaging in light-induced electron transfer. The molar ratio of ligand to $TiCl_4$ remains constant during synthesis: controlled addition of a toluene solution of $TiCl_4$ to a solution of L in the same solvent yields a homogeneous precursor mixture that solidifies quantitatively upon solvent evaporation.

Upon exposure to atmospheric moisture, spontaneous hydrolysis of Ti–Cl bonds produces mono- and bis-hydrated complexes in equilibrium with titanium oxychloride ($TiCl_2O$). These hydrolyzed species form the redox-active foundation of the photocatalytic cycle. Partial internal reduction accompanies hydrolysis, generating mixed-valent Ti(IV)/Ti(III) centers linked through Ti–O–Ti or Ti–OH bridges—sites that are intrinsically predisposed to activate small molecules.

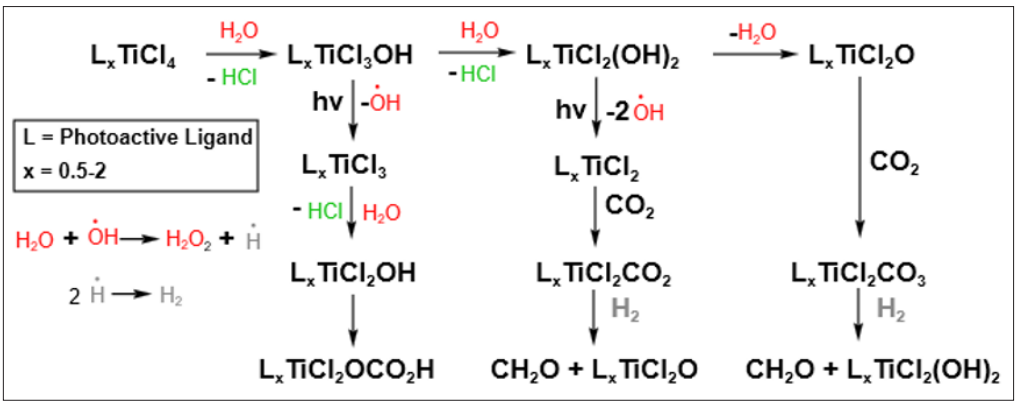

Figure 3: Stage 2-Universal Photochemical Equilibrium: Visible-Light Activation of Ti–OH units Within Hydrolyzed Ti–ligand Matrices Releases Hydroxyl Radicals (•OH) that Simultaneously Regenerate Reduced Ti Sites and Reduce Captured CO_2 into Formaldehyde, Marking the onset of Reactive DAC

Atmospheric CO_2 is captured spontaneously by these hydrolyzed titanium species, yielding carbonate and bicarbonate intermediates that bind within the Ti–O framework. According to the U.S. Department of Energy's classification, this behavior constitutes reactive direct air capture (Reactive DAC), wherein CO_2 fixation and its in-situ transformation occur within a single material phase.

Illumination triggers the formation of hydroxyl radicals via Ti–OH bond photolysis. 3 These radicals-and molecular hydrogen concurrently generated through radical–water interactions-drive the reduction of carbonate intermediates to formaldehyde (HCHO). The emergence of formaldehyde, consistently detected across all systems, is the defining chemical signature of Stage 2 and marks the first stable product of CO_2 fixation within the hydrolyzed Ti–O network.

This hydrolytic–redox pathway operates autonomously, independent of ligand identity, confirming its universality. Nevertheless, the ligand profoundly influences how the reaction medium evolves: π-bonded systems such as PI favor charge delocalization and extended redox communication, whereas σ-donating chelates like phen or BZX impose greater structural order and controlled proton management. Thus, while the mechanistic core—CO_2 capture, hydrolytic reduction, and formaldehyde formation—is common to all, the ligand environment dictates the architecture, photochemical responsiveness, and ultimate direction of subsequent transformations leading to higher carbon products or, in the case of phen, to polyoxymethylene (POM).

Stage 3: Ligand-Directed Product Evolution

The third and final stage represents the culmination of the entire catalytic sequence—the moment when the initially hydrolyzed Ti–ligand matrix becomes a fully autonomous photochemical system. Under continuous illumination, the matrix reorganizes into self-sustaining coordination environments in which electron transfer, proton exchange, and radical generation occur in perpetual balance. At this point, catalysis proceeds **without interruption**, driven solely by light and atmospheric inputs (CO_2, H_2O, and O_2). Product evolution is no longer a stochastic outcome of hydrolysis but a *programmed transformation* encoded in the electronic structure of the Ti–ligand ensemble. Each ligand dictates its own trajectory of reorganization, channeling the redox and radical dynamics toward a distinct family of carbon products.

Each ligand dictates its own trajectory of reorganization, channeling the redox and radical dynamics toward a distinct family of carbon products. Beyond these electronic and redox effects, weak noncovalent interactions also play a subtle yet cohesive role in sustaining the photochemical matrix. Although the reactivity of the ligand–$TiCl_4$ and hydrolyzed Ti–oxo complexes is governed primarily by coordination and redox processes, van der Waals forces contribute to the overall assembly and stability of the system. Dispersion interactions between the aromatic π-surfaces of 2-phenylindole, 2-phenylbenzoxazole, or 1,10-phenanthroline ligands and the polarizable $TiCl_4$ center assist the initial pre-organization required for efficient coordination. Within the hydrolyzed Ti–OH network, weak intermolecular attractions between adjacent Ti–oxo units and bound solvent molecules promote the formation of dynamic, redox-active aggregates. Furthermore, van der Waals interactions facilitate the physisorption of CO_2 and H_2O at the matrix interface, enhancing gas capture under ambient conditions. Thus, while secondary in strength, these forces act as a cohesive component that supports ligand-directed self-assembly and the maintenance of the photocatalytically active Ti–oxo framework.

Product Formation in the 2-Phenylindole–$TiCl_4$ (PI·$TiCl_4$) System

In the PI·$TiCl_4$ assembly, the active species is an **α-ketocarboxylate titanium complex (complex 16**, Figure 4) formed *in situ* by **CO insertion into a Ti–C bond** of a carbonated intermediate derived from the hydrolyzed 2-phenylindolenine–$TiCl_4$ matrix. This transformation marks the onset of the continuous, self-sustaining photocatalytic phase.

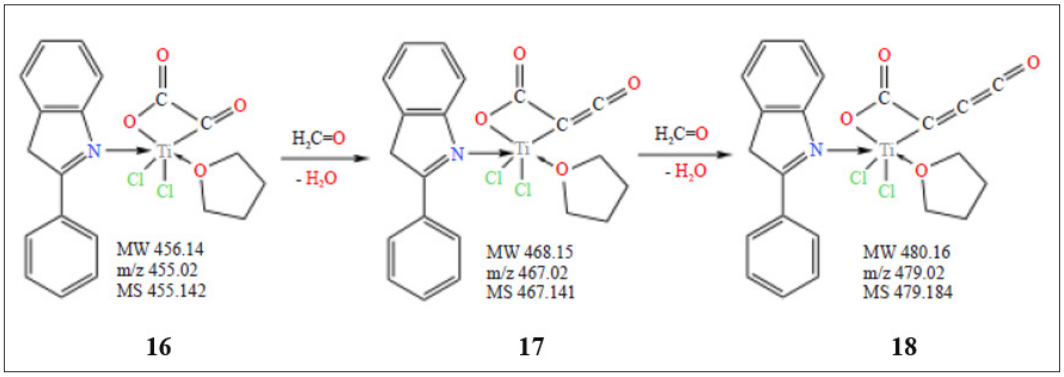

Figure 4: Stage 3 in the PI–$TiCl_4$ pathway: Visible-light-Induced Hydroxyl-Radical Flux Channels Formaldehyde into α-ketocarboxylate Titanium Complexes, Establishing a Self-propagating Redox Loop That Extends Carbon Chains and Defines the Reactive DAC Chemistry of the System

Upon irradiation, **complex 16** undergoes **dehydrative condensation** between its α-keto group and photogenerated formaldehyde, yielding a **ketene intermediate (complex 17)**. Sequential one-carbon extensions produce **complex 18**, which subsequently undergoes **photo-hydrogenation** of the pendant carbon chain to form an **α-aldehyde**. Within this dynamic matrix, all these transformations—carbonyl coupling, hydrogen transfer, and Ti redox cycling—occur cooperatively under light excitation, requiring no external reagents or redox mediators.

At this final stage, **hydroxyl radicals act as both initiators and regulators of continuous turnover**.

- Through **hydrogen abstraction** from aldehydic intermediates, they generate carbon-centered radicals that promote **C–C coupling** among C_6–C_9 fragments.
- Simultaneously, they **regenerate reduced Ti^{3+} centers**, closing the internal redox loop and enabling indefinite catalytic operation under illumination.

The result is a **continuous photochemical cascade** that spontaneously builds higher-carbon oxygenates (C_{12}–C_{19}), dominated by **C_{16} species** bearing both aldehyde and carboxylate termini. This outcome demonstrates that once Stage 3 is reached, the system functions as a **self-propagating artificial photosynthetic network**, in which hydroxyl-radical chemistry, ligand π-stabilization, and Ti redox cycling operate in unbroken synergy. Full details may be obtained from the original publication. (Citation)

This uninterrupted operation distinguishes the PI–$TiCl_4$ system as the first example of a **continuously regenerative, light-driven carbon-chain-building process** emerging spontaneously from a hydrolyzed organotitanium complex.

Stage 3: Product Formation in the 2-Phenylbenzoxazole–$TiCl_4$ (BZX·$TiCl_4$) System

In contrast to the **PI·$TiCl_4$** system, where a discrete Ti-centered α-ketocarboxylate complex drives reductive carbon-chain extension, the **BZX·$TiCl_4$** assembly operates through a **ligand-centered photochemical cascade**. Here, the active species arises not from Ti–C bond transformations but from redox activation and structural reorganization of the ligand itself.

Following hydrolytic activation, the σ-bonded **2-phenylbenzoxazole–$TiCl_4$** complex evolves into a **mixed-valent Ti^{3+}/Ti^{4+} hydroxo–oxo equilibrium**, capable of reversible electron exchange with the aromatic ligand. This configuration provides a dynamic redox interface between the titanium core and the π-system of benzoxazole, establishing the conditions for photoinduced ligand reduction.

Upon visible-light irradiation, **photoelectron transfer** from the Ti–O framework reduces coordinated **benzoxazole** to its benzoxazoline form. The reduced ligand reacts spontaneously with atmospheric CO_2, forming a **benzoxazoline carbonate intermediate**, which subsequently undergoes **hydrogenation**—mediated by in situ H_2 derived from hydroxyl-radical reactions—to yield a **formylated benzoxazole derivative** (Figure 5).

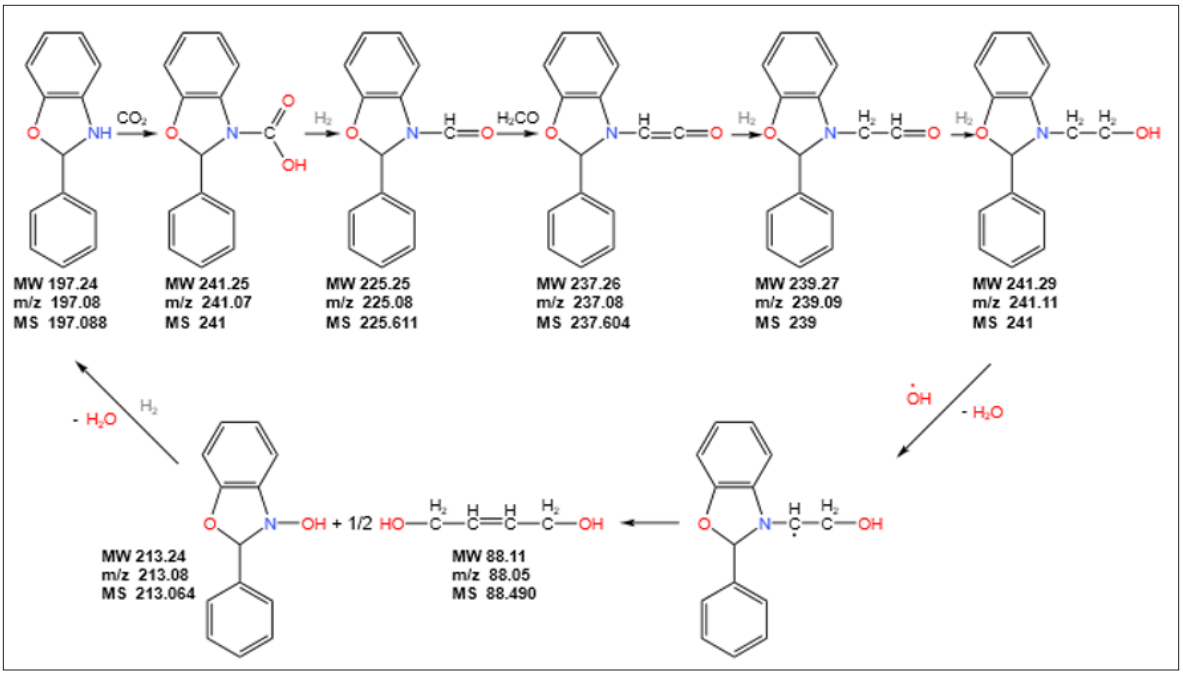

Figure 5: Stage 3 in the BZX–$TiCl_4$ pathway: visible-light–activated hydroxyl radicals mediate ligand-directed molecular assembly accompanied by selective hydrogenation of 2-phenylbenzoxazole to benzoxazoline a self-terminating transformation that stabilizes the photocatalytic matrix.

This derivative acts as the **ligand-derived photocatalytic relay**, orchestrating a sequence of **formyl transfer, aldol-type condensation, and oxidative coupling** steps that produce oxygenated intermediates in the **C_4–C_8 range**, bearing **hydroxyl, carbonyl, and carboxylic acid functionalities**. Within the Ti–O redox network, **hydroxyl radicals** generated by Ti–OH photolysis sustain the continuous turnover of these transformations, promoting **dehydrogenation** and **oxygen insertion** while regenerating the Ti^{3+} sites that maintain the redox cycle.

Unlike the PI system, which progresses toward **reductive dimerization and C-chain elongation**, the **BZX·$TiCl_4$** system follows an **oxidative, self-limiting trajectory**, terminating in short, oxygen-rich products. This divergence reflects the ligand's σ-bonded coordination mode and its higher electron affinity, which favor radical oxidation over coupling.

Thus, the **BZX·$TiCl_4$** pathway constitutes the **oxidative branch** of the *Arzoumanidis artificial photosynthesis platform* a complementary mode to the **reductive, Ti-centered, carbon-growth mechanism of PI·$TiCl_4$**. Together, these two pathways exemplify the dual functionality of the hydrolyzed organotitanium framework: a single chemical foundation capable of operating continuously under light, yet bifurcating into distinct *oxidative* or *reductive* outcomes according to the ligand's electronic nature.

Stage 3 – Product Formation in the 1,10-Phenanthroline–$TiCl_4$ (Phen·$TiCl_4$) System

In the **Phen·$TiCl_4$** system, photochemical excitation triggers a transition from molecular to multinuclear reactivity, leading to the formation of **binuclear titanium species**, primarily *phen·Ti_2Cl_5* and *phen·Ti_2Cl_7*, under mildly hydrolytic and reducing conditions [13]. These mixed-valent Ti^{3+}/Ti^{4+} assemblies characterized in the original study—constitute the fundamental photochemical

units of this system. Within their coordination sphere, **formic acid** emerges as the decisive reactive component, binding to the titanium centers to form **Ti–formate complexes** that direct the downstream chemistry.

Upon illumination, **formaldehyde**, generated during Stage 2, is activated within this multinuclear Ti–formate environment to **·CH_2O radicals**. These radicals undergo **stepwise oligomerization** within the confined coordination domain, producing a continuum of **polyoxymethylene-type species**, formally expressed as **$HCOO(CH_2O)_nH$**, where n ranges approximately from 3 to 30. The process is entirely radical-driven and **autonomously regenerative**: each propagation event regenerates Ti^{3+} centers and sustains further radical initiation under constant illumination.

The phen ligand, partially protonated to $phenH^+$, performs several critical functions:

- It maintains **intervalent electronic coupling** between the Ti^{3+} and Ti^{4+} sites,
- It facilitates **proton-coupled electron transfer (PCET)**, and
- It stabilizes reactive radical intermediates through π-stacking and electrostatic confinement.

Through this cooperative architecture, the Phen·$TiCl_4$ matrix operates as a self-sustaining radical polymerization network, rather than a chain-growth condensation system. The reaction does not extend carbon length via aldol processes but instead oligomerizes formaldehyde through Ti-mediated radical propagation yielding polyoxymethylene (POM) as the dominant photochemical product.

This pathway thus defines the stabilized, energy-storage branch of the Arzoumanidis artificial photosynthesis platform: a continuous, light-driven radical cascade that transforms CO_2 and H_2O into polymeric oxygenates via the Ti–formate intermediate [14]. Together with the reductive PI and oxidative BZX systems, the Phen·$TiCl_4$ complex completes the triad of autonomous photocatalytic modes each continuously operating yet uniquely tuned by its ligand's coordination and redox behavior.

Across the three ligand-defined titanium systems, the final photochemical stage evolves into distinct yet interdependent routes of CO_2 transformation. The PI·$TiCl_4$ complex represents the reductive branch, where hydroxyl-radical-initiated Ti^{3+} centers drive the sequential reduction of CO_2 to formaldehyde and short oxygenates. The BZX·$TiCl_4$ complex defines the oxidative branch, in which the ligand's σ-donor oxygen functionality amplifies Ti–OH bond activation, enabling deep oxidation and selective C–C coupling chemistry. The Phen·$TiCl_4$ complex, by contrast, establishes the stabilized radical-propagation branch a continuously operating, light-driven engine that converts formaldehyde into polyoxymethylene (POM) through a self-regenerating Ti–formate network.

Together, these systems constitute a modular artificial photosynthesis platform, capable of autonomous CO_2 and H_2O conversion under ambient conditions. Each branch performs a specific photochemical function reduction, oxidation, or polymerization yet all operate through the universal mechanism of Ti–OH photolysis, hydroxyl-radical generation, and mixed-valent electron transfer. This convergence of pathways demonstrates that by controlling the hydrolysis state and redox activity of titanium through ligand design, it is possible to construct continuous, self-maintaining photochemical cycles that capture, reduce, and store atmospheric carbon as stable organic frameworks.

Conclusion and Outlook

The combined results obtained with the three ligand systems—2-phenylindole (PI), 2-phenylbenzoxazole (BZX), and 1,10-phenanthroline (Phen) define a coherent and universal framework for light-driven CO_2 capture and conversion by hydrolyzed titanium complexes. Each ligand dictates a distinct mode of structural and electronic self-organization within the titanium coordination sphere, establishing complementary photochemical functions. In the π-bonded PI–$TiCl_4$ system, radical-induced ligand metallation and extended charge delocalization drive a reductive carbon-growth sequence culminating in long-chain oxygenates. The σ-bonded BZX–$TiCl_3OH$ complex promotes stabilization of Ti–OH and Ti–O• species, initiating oxidative ligand-centered CO_2 activation and selective C–C coupling. Meanwhile, the Phen–$TiCl_4$ matrix sustains visible-light-induced photoredox cycling through mixed-valent Ti^{3+}/Ti^{4+} dimerization, enabling radical propagation and formaldehyde oligomerization into polyoxymethylene.

Together, these systems converge to outline the Arzoumanidis Artificial Photosynthesis Framework a unifying chemical principle in which hydrolyzed organotitanium matrices function as self-organizing, redox-active scaffolds capable of autonomous CO_2 and H_2O conversion under ambient conditions. This discovery overturns the long-standing view that hydrolysis deactivates metal halides: instead, controlled hydrolysis emerges as the key enabling process that generates dynamic Ti–O–Ti and Ti–OH networks, fostering continuous photochemical function through spontaneous structural reorganization and self-regeneration.

The universality of this behavior across three distinct ligand classes demonstrates that the phenomenon arises not from the ligands themselves, but from the intrinsic reactivity of the Ti–O–C network—an emergent photochemical order in simple inorganic–organic hybrids. The implication is profound: by harnessing the natural hydrolysis–redox equilibrium of titanium, it becomes possible to construct molecularly adaptive photocatalysts that combine the selectivity of coordination chemistry with the resilience of materials science.

Looking forward, this framework offers a practical foundation for scalable, autonomous CO_2 utilization technologies. Modular Ti–ligand matrices can be tailored to favor reductive, oxidative, or polymerization-type carbon pathways, integrated into photochemical flow systems or thin-film reactors operating solely under sunlight and ambient moisture. With further optimization of ligand architecture, hydrolysis control, and light-harvesting design, such systems could achieve continuous solar-to-chemical conversion without external bias or semiconductor interfaces.

Beyond its immediate application, the framework introduces a broader concept—the chemistry of self-organizing photochemical matter—in which light, water, and a redox-active metal co-evolve into a self-sustaining reaction matrix. This principle bridges molecular catalysis, materials evolution, and the first operational model of autonomous artificial photosynthesis based entirely on earth-abundant elements.

Author Contributions

G.G.A. conceived the study, interpreted the experimental data, and wrote the manuscript with contributions from both authors. M.P. performed experimental work and selected the analytical methods.

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Notes

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