ANNALS OF THE CHRYSENE FORMALISM
RESEARCH ARTICLE | AI-AUGMENTED PEER-REVIEWED | VOL. 1, NO. 1 | SEPTEMBER 2026

Electronic and Kinetic Feasibility of a 3, 6, 9, 12-Connected Rectangular Chrysene Network for Pt-Assisted Hydrogen Evolution: A Conditional Comparison with a Dibenzochrysene Kagome Benchmark

Charles D. Schaper, Ph.D.
Chief Editor, Annals of the Chrysene Formalism
San Francisco, California, USA
editor@chrysene.com

Abstract

A dibenzo[g, p]chrysene-based, sp^2-carbon-linked covalent organic framework provides experimental precedent for visible-light hydrogen evolution under platinum-assisted, sacrificial-donor conditions. That result does not establish whether a network formed from 3, 6, 9, 12-functionalized chrysene nodes will inherit the necessary optical, charge-separation, transport, and redox properties. We formulate a falsifiable feasibility analysis for a rectangular candidate in which N-segment bridges connect C3(i, j) to C9$(i + 1, j)$, while $(N + 2)$-segment bridges connect C12(i, j) to C6$(i, j + 1)$, with $N \in 2\mathbb{Z}_{\geq 0}$. Green's-function reduction gives distinct directional couplings $T_x(E)$ and $T_y(E)$. Within a scalar nearest-neighbor model, $T_x(E_*)T_y(E_*) \neq 0$ implies nonzero Bloch dispersion in both in-plane directions, with bandwidth $4(|T_x| + |T_y|)$. Electronic connectivity is combined with independent requirements for useful absorption, robustly favorable charge-separation and hydrogen-reduction free energies, carrier survival, diffusion to an accessible platinum site, and interfacial electron injection. These quantities yield an explicit lower bound $R_{\mathfrak{R}}^{\mathrm{LB}}$ on the mass-normalized hydrogen-evolution rate. Feasibility is defined by the experimentally testable inequality

$$R_{\mathfrak{R}}^{\mathrm{LB}} > R_{\mathrm{LOQ}},$$

where R_{LOQ} is an independently determined, background-corrected limit of quantification; performance equal to the DBC benchmark is not required. An optional metal-conditioned extension describes how Mg or redox-active transition-metal states may modify energetic alignment while imposing an additional excited-state quenching constraint. The analysis supports prospective testing of the hydrogen-evolution half-reaction relevant to artificial photosynthesis, but does not establish catalyst-free hydrogen production, water oxidation, or overall water splitting.

Keywords: substituted chrysene; covalent organic frameworks; rectangular molecular networks; artificial photosynthesis; photocatalytic hydrogen evolution; anisotropic electronic coupling; Green's-function reduction; charge separation; carrier diffusion; metal-conditioned materials; dibenzochrysene; detectability bounds.

1 Introduction

The conversion of solar radiation into a storable chemical fuel requires a sequence of distinct physical and chemical operations. A photoactive material must absorb incident photons, form electronically excited states, separate charge, transport the resulting reducing equivalents, and deliver electrons to a catalytic site before recombination occurs. For hydrogen production, the terminal reductive half-reaction is

$$2H^+ + 2e^- \longrightarrow H_2. \tag{1}$$

Absorption is therefore necessary but not sufficient. A material that absorbs visible light may nevertheless fail because its excited state is localized, its charge-separated state is thermodynamically inaccessible, its carriers recombine too rapidly, or its electrons cannot reach an accessible hydrogen-evolution catalyst.

A dibenzo[g, p]chrysene-based, sp^2-carbon-linked covalent organic framework, denoted below by $\mathfrak{K}$, provides a relevant experimental benchmark. The reported DBC-sp^2c-COF has kagome connectivity and supports visible-light hydrogen evolution in the presence of ascorbic acid as a sacrificial electron donor and platinum as a cocatalyst [YHW+25]. Spectroscopic

Citation: Schaper, C. D. (2026). Electronic and Kinetic Feasibility of a 3, 6, 9, 12-Connected Rectangular Chrysene Network for Pt-Assisted Hydrogen Evolution: A Conditional Comparison with a Dibenzochrysene Kagome Benchmark *Annals of the Chrysene Formalism*, 1(1), 414–436. https://chrysene.com/index.php/acf/article/view/36 • First published by Schaper Systems Press in the *Annals of the Chrysene Formalism*, Vol. 1, No. 1 (2026).

measurements and electronic-structure calculations reported for that material associate its activity with a planar conjugated structure, donor–acceptor interactions, charge generation, charge separation, and carrier transport. The DBC result demonstrates that a chrysene-related fused aromatic node can participate in a conjugated photocatalytic framework. It does not imply that a different chrysene node or network topology inherits the same activity.

The candidate considered here is a periodic network formed from 3, 6, 9, 12-functionalized chrysene nodes. Let

$$N \in 2\mathbb{Z}_{\geq 0}$$

be fixed. In the first crystallographic direction, the attachment rule is

$$\mathrm{C3}(i, j) \longleftrightarrow \mathrm{C9}(i + 1, j), \tag{2}$$

through a bridge containing N effective conjugated segments. In the second direction, the rule is

$$\mathrm{C12}(i, j) \longleftrightarrow \mathrm{C6}(i, j + 1), \tag{3}$$

through a bridge containing $N + 2$ segments. The unequal bridge orders produce a rectangular, rather than metrically square, periodic network. We denote this candidate by

$$\mathfrak{R}_N.$$

Its primitive translation lengths, directional electronic couplings, effective masses, and charge-transport scales need not be equal.

The purpose of the present work is not to establish that $\mathfrak{R}_N$ performs as well as $\mathfrak{K}$. Instead, we consider the weaker and experimentally more relevant feasibility question:

> *Under what explicit geometric, electronic, thermodynamic, and kinetic inequalities would the rectangular* 3, 6, 9, 12*-connected chrysene network be expected to produce a nonzero and experimentally detectable hydrogen signal under the Pt-assisted sacrificial-donor conditions of the DBC benchmark?*

This formulation replaces a qualitative analogy with a collection of computable and measurable conditions. In particular, no lower bound is inferred from the common chrysene character alone.

The analysis begins by assigning distinct bridge Hamiltonians to the N- and $N + 2$-segment directions. Elimination of the bridge degrees of freedom gives the effective couplings

$$T_x(E) = \mathbf{v}_3^{\dagger}\big(EI - H_{\mathrm{B}}^{(N)}\big)^{-1}\mathbf{v}_9, \qquad T_y(E) = \mathbf{v}_{12}^{\dagger}\big(EI - H_{\mathrm{B}}^{(N+2)}\big)^{-1}\mathbf{v}_6.$$

The condition

$$T_x(E)T_y(E) \neq 0$$

is shown to be sufficient for nonzero dispersion in both in-plane directions within the reduced nearest-neighbor model. This condition does not prove macroscopic mobility, but it excludes an electronically disconnected or strictly one-dimensional realization at the comparison energy.

Electronic connectivity is then combined with separate thermodynamic conditions. Charge separation and delivery of an electron toward the H^+/H_2 couple require finite energetic margins, written schematically as

$$\Delta G_{\mathrm{CS}} \leq -\delta_{\mathrm{CS}} < 0, \qquad \Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}} < 0.$$

The positive margins δ_{CS} and δ_{H} prevent numerical uncertainty from being hidden inside marginal equalities. Transport is constrained independently by requiring that the directional charge-diffusion length reach an accessible platinum site before recombination.

The principal contributions of this work are as follows:

1. the 3, 6, 9, 12-connected candidate is defined as an anisotropic rectangular lattice with N- and $N + 2$-segment bridges;
2. explicit Green's-function criteria are given for nonzero electronic coupling in both lattice directions;
3. the rectangular Bloch dispersion, bandwidth, group velocities, and transport-anisotropy parameters are derived;
4. charge-separation, hydrogen-reduction, diffusion-length, and catalyst-access inequalities are stated as independent feasibility conditions; and
5. these conditions are combined into a lower bound $R^{\mathrm{LB}}_{\mathfrak{R}_N}$ on the hydrogen-evolution rate, with predicted detectability defined by
$$R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}}, \tag{4}$$
where R_{LOQ} is the independently determined experimental limit of quantification.

Equation (4) is deliberately weaker than a non-inferiority comparison with the DBC material. The candidate may satisfy the feasibility criterion even when

$$R_{\mathfrak{R}_N} \ll R_{\mathfrak{K}}.$$

Conversely, geometric density, visible absorption, or nonzero bandwidth alone cannot satisfy the criterion.

The scope remains restricted to Pt-assisted hydrogen evolution with a sacrificial electron donor. Water oxidation, oxygen evolution, catalyst-free proton reduction, and integrated overall water splitting are not inferred. A bounded metal-conditioned extension is considered only as a possible means of modifying electronic alignment or charge-transfer energetics. The resulting analysis is therefore a falsifiable feasibility framework for the reductive half-reaction relevant to artificial photosynthesis, rather than a demonstration of a complete artificial-photosynthetic device.

2 DBC Benchmark and Scope

Definition 1 (DBC benchmark)**.** *Let $\mathfrak{K}$ denote the dibenzo[g, p]chrysene-based DBC-sp^2c-COF reported by Yu et al. [YHW⁺25]. The material is a two-dimensional, sp^2-carbon-linked covalent organic framework with kagome connectivity and stacked conjugated layers. Its aromatic nodes are derived from* 2, 7, 10, 15*-functionalized dibenzo[g, p]chrysene.*
Under visible-light irradiation, ascorbic acid as a sacrificial electron donor, and 0.8 wt % *photodeposited platinum, the reported material exhibited the mass-normalized hydrogen-evolution rate*

$$R_{\mathrm{H_2},\mathfrak{K}} = 172.93\,\mathrm{mmol\,g^{-1}\,h^{-1}},$$

together with an apparent quantum yield

$$\mathrm{AQY}_{\mathfrak{K}}(420\,\mathrm{nm}) = 14.9\%.$$

These values are regarded as experimental data belonging to $\mathfrak{K}$; they are not assigned to the candidate network.

Definition 2 (Rectangular chrysene candidate)**.** *For a fixed*

$$N \in 2\mathbb{Z}_{\geq 0},$$

let $\mathfrak{R}_N$ denote the idealized periodic network formed from 3, 6, 9, 12*-functionalized chrysene nodes with attachment rules*

$$\mathrm{C3}(i, j) \longleftrightarrow \mathrm{C9}(i + 1, j)$$

through an N-segment conjugated bridge and

$$\mathrm{C12}(i, j) \longleftrightarrow \mathrm{C6}(i, j + 1)$$

through an $(N + 2)$-segment conjugated bridge. No synthesis, crystallinity, charge separation, or hydrogen-evolution result is assumed for $\mathfrak{R}_N$.

Definition 3 (Matched hydrogen-evolution boundary)**.** *The formal reaction boundary is the tuple*

$$\mathscr{C}_{\mathrm{HER}} = \left(\mathrm{H_2O}, D_{\mathrm{sac}}, C_{\mathrm{Pt}}, T, \mathrm{pH}, I_\lambda\right),$$

where D_{sac} is the sacrificial electron donor, C_{Pt} denotes the platinum loading and deposition state, T is temperature, and I_λ is the incident spectral irradiance. In correspondence with the DBC experiment,

$$D_{\mathrm{sac}} = 0.1\,\mathrm{M}\ \textit{ascorbic acid}, \qquad C_{\mathrm{Pt}} = 0.8\,\mathrm{wt}\,\%,$$

with visible irradiation satisfying

$$\lambda > 420\,\mathrm{nm}.$$

Hypothesis 1 (Matched reaction boundary)**.** *Whenever $\mathfrak{R}_N$ and $\mathfrak{K}$ are compared, they are assigned the same formal boundary condition $\mathscr{C}_{\mathrm{HER}}$. Thus, differences in predicted response are not attributed to different sacrificial donors, platinum loadings, illumination windows, temperatures, or proton activities.*

Remark 1 (Role of the DBC result)**.** *The DBC observation supplies three forms of precedent: a chrysene-related fused aromatic node can be incorporated into a conjugated periodic framework; such a framework can support charge generation and separation; and its photogenerated electrons can reach a platinum hydrogen-evolution site. None of these observations establishes the corresponding property for $\mathfrak{R}_N$. The benchmark therefore defines a mechanistically relevant comparison class rather than an inherited performance value.*

Definition 4 (Detectable feasibility)**.** *Let $R_{\mathrm{LOQ}} > 0$ denote the hydrogen-evolution rate corresponding to the limit of quantification of the prospective analytical method. The candidate $\mathfrak{R}_N$ is said to be* analytically feasible for detectable sacrificial hydrogen evolution *if the model establishes a lower bound $R^{\mathrm{LB}}_{\mathfrak{R}_N}$ satisfying*

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}}.$$

This definition imposes no requirement that

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} \geq R_{\mathrm{H_2},\mathfrak{K}}.$$

Remark 2 (Excluded conclusions)**.** *The present comparison does not establish:*

1. *catalyst-free proton reduction;*
2. *oxidation of water to molecular oxygen;*
3. *sacrificial-donor-free or overall water splitting;*
4. *a quantitative hydrogen-evolution rate before the required candidate-specific parameters are determined;*
5. *equality or non-inferiority relative to the DBC benchmark; or*
6. *the synthetic accessibility or thermodynamic stability of the idealized rectangular lattice.*

Ascorbic acid removes photogenerated oxidizing equivalents, while platinum supplies the terminal proton-reduction site. Accordingly, the modeled experiment concerns the reductive half-reaction relevant to artificial photosynthesis, not a complete artificial-photosynthetic cycle.

The subsequent analysis determines sufficient inequalities for absorption, two-direction electronic coupling, charge separation, carrier survival, catalyst access, and proton-reduction energetics. Its logical objective is to decide whether those measurable inequalities can imply

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}},$$

without presupposing the experimental conclusion that the candidate already evolves hydrogen.

3 Rectangular Geometry and Density

Let

$$\mathbf{e}_x = (1,0), \qquad \mathbf{e}_y = (0,1)$$

denote the standard basis of $\mathbb{R}^2$. For fixed $N \in 2\mathbb{Z}_{\geq 0}$, let $a_N > 0$ and $b_{N+2} > 0$ denote, respectively, the center-to-center distances between adjacent chrysene nodes in the C3–C9 and C12–C6 directions. These quantities are geometric parameters to be obtained from an optimized periodic structure; they are not assumed to be proportional to the nominal segment counts.

Definition 5 (Rectangular translation lattice)**.** *The translation lattice of* $\mathfrak{R}_N$ *is*

$$\Lambda_N = a_N\mathbb{Z}\,\mathbf{e}_x \oplus b_{N+2}\mathbb{Z}\,\mathbf{e}_y.$$

The node indexed by $(i,j) \in \mathbb{Z}^2$ *is embedded at*

$$\mathbf{r}_{i,j} = i a_N \mathbf{e}_x + j b_{N+2}\mathbf{e}_y.$$

A primitive cell is the half-open rectangle

$$\mathcal{U}_N = [0, a_N) \times [0, b_{N+2}),$$

whose area is

$$A_N = \mathrm{Area}(\mathcal{U}_N) = a_N b_{N+2}.$$

Definition 6 (Node and edge sets)**.** *The embedded rectangular graph is*

$$\mathcal{G}_{\mathfrak{R}_N} = \left(V_{\mathfrak{R}_N}, E_{\mathfrak{R}_N}\right),$$

where

$$V_{\mathfrak{R}_N} = \left\{v_{i,j} : (i,j) \in \mathbb{Z}^2\right\}$$

and

$$E_{\mathfrak{R}_N} = E_x \sqcup E_y,$$

with

$$E_x = \left\{\{v_{i,j}, v_{i+1,j}\} : (i,j) \in \mathbb{Z}^2\right\},$$

$$E_y = \left\{\{v_{i,j}, v_{i,j+1}\} : (i,j) \in \mathbb{Z}^2\right\}.$$

Edges in E_x *represent the* N*-segment* C3–C9 *bridges, whereas edges in* E_y *represent the* $(N+2)$*-segment* C12–C6 *bridges.*

Proposition 1 (Primitive-cell counts)**.** *The quotient graph* $\mathcal{G}_{\mathfrak{R}_N}/\Lambda_N$ *contains one node and two undirected edges. Every node of* $\mathcal{G}_{\mathfrak{R}_N}$ *has coordination number four.*

Proof. Translation by Λ_N identifies every $v_{i,j}$ with $v_{0,0}$, so the quotient contains one node. One representative of each directional edge orbit is

$$\{v_{0,0}, v_{1,0}\} \quad \text{and} \quad \{v_{0,0}, v_{0,1}\}.$$

In the infinite graph, $v_{i,j}$ is adjacent to

$$v_{i-1,j}, \quad v_{i+1,j}, \quad v_{i,j-1}, \quad v_{i,j+1},$$

and therefore has degree four. □

Definition 7 (Areal densities)**.** *The areal node density and areal crossbar density of* $\mathfrak{R}_N$ *are*

$$\rho^{(A)}_{\mathfrak{R}_N} := \frac{1}{a_N b_{N+2}}$$

and

$$\rho^{(A)}_{E,\mathfrak{R}_N} := \frac{2}{a_N b_{N+2}},$$

respectively. If the bridge orders are counted by their effective segment numbers, the corresponding segment density is

$$\rho^{(A)}_{\mathrm{seg},\mathfrak{R}_N} := \frac{N + (N+2)}{a_N b_{N+2}} = \frac{2N+2}{a_N b_{N+2}}.$$

For the kagome benchmark $\mathfrak{K}$, let $d_{\mathfrak{K}} > 0$ denote the nearest-neighbor node distance. A primitive kagome cell has area

$$A_{\mathfrak{K}} = 2\sqrt{3}\, d_{\mathfrak{K}}^2$$

and contains three nodes. Hence,

$$\rho^{(A)}_{\mathfrak{K}} = \frac{3}{2\sqrt{3}\, d_{\mathfrak{K}}^2} = \frac{\sqrt{3}}{2 d_{\mathfrak{K}}^2}.$$

Proposition 2 (Rectangular-to-kagome density ratio)**.** *The areal node-density ratio satisfies*

$$\boxed{\frac{\rho^{(A)}_{\mathfrak{R}_N}}{\rho^{(A)}_{\mathfrak{K}}} = \frac{2 d_{\mathfrak{K}}^2}{\sqrt{3}\, a_N b_{N+2}}}.$$

Consequently,

$$\rho^{(A)}_{\mathfrak{R}_N} > \rho^{(A)}_{\mathfrak{K}}$$

if and only if

$$a_N b_{N+2} < \frac{2}{\sqrt{3}} d_{\mathfrak{K}}^2.$$

Proof. Substitution of

$$\rho^{(A)}_{\mathfrak{R}_N} = \frac{1}{a_N b_{N+2}} \quad \text{and} \quad \rho^{(A)}_{\mathfrak{K}} = \frac{\sqrt{3}}{2d_{\mathfrak{K}}^2}$$

gives the stated ratio. The inequality follows because all geometric parameters are strictly positive. □

Corollary 1 (Square limit)**.** *If*

$$a_N = b_{N+2} = d_{\mathfrak{R}},$$

then

$$\frac{\rho^{(A)}_{\mathfrak{R}_N}}{\rho^{(A)}_{\mathfrak{K}}} = \frac{2}{\sqrt{3}} \left(\frac{d_{\mathfrak{K}}}{d_{\mathfrak{R}}}\right)^2,$$

which is the density relation for the isotropic square realization.

Remark 3 (Interpretive limitation)**.** *For finite positive a_N and b_{N+2},*

$$\rho^{(A)}_{\mathfrak{R}_N} > 0,$$

so the idealized material contains a finite areal density of photoactive nodes and conjugated crossbars. Neither positivity nor superiority of this geometric density implies nonzero charge separation or hydrogen evolution. Comparison with the mass-normalized DBC rate additionally requires the molecular mass of the node and the two directional bridges. The corresponding mass-normalized expressions are therefore deferred to the Supplementary Information.

4 Direction-Dependent Electronic Coupling

The unequal bridge orders in $\mathfrak{R}_N$ require separate electronic reductions in the two crystallographic directions. Let

$$m_x = N, \qquad m_y = N + 2,$$

and define the associated attachment-site pairs by

$$(p_x, q_x) = (3, 9), \qquad (p_y, q_y) = (12, 6).$$

Definition 8 (Directional bridge spaces and resolvents)**.** *For $\mu \in \{x, y\}$, let*

$$\mathcal{H}_{\mathrm{B},\mu}$$

be the finite-dimensional frontier-orbital space of the m_μ-segment bridge, and let

$$H_{\mathrm{B},\mu} = H_{\mathrm{B}}^{(m_\mu)} : \mathcal{H}_{\mathrm{B},\mu} \longrightarrow \mathcal{H}_{\mathrm{B},\mu}$$

be its Hermitian bridge Hamiltonian. For

$$E \notin \mathrm{Spec}(H_{\mathrm{B},\mu}),$$

define the bridge resolvent

$$G_{\mathrm{B},\mu}(E) := \left(EI - H_{\mathrm{B},\mu}\right)^{-1}.$$

Let $|\psi_{p_\mu}\rangle$ and $|\psi_{q_\mu}\rangle$ denote the effective frontier states of the two adjacent chrysene nodes. Their couplings to the bridge are represented by vectors

$$\mathbf{v}_{p_\mu}, \mathbf{v}_{q_\mu} \in \mathcal{H}_{\mathrm{B},\mu}.$$

Before elimination of the bridge degrees of freedom, the corresponding node–bridge–node Hamiltonian has the block form

$$H_\mu = \begin{pmatrix} \varepsilon_{p_\mu} & \mathbf{v}_{p_\mu}^\dagger & 0 \\ \mathbf{v}_{p_\mu} & H_{\mathrm{B},\mu} & \mathbf{v}_{q_\mu} \\ 0 & \mathbf{v}_{q_\mu}^\dagger & \varepsilon_{q_\mu} \end{pmatrix}. \tag{5}$$

Definition 9 (Directional effective coupling)**.** *The Green's-function reduction of (5) defines*

$$T_\mu(E) := \mathbf{v}_{p_\mu}^\dagger G_{\mathrm{B},\mu}(E) \mathbf{v}_{q_\mu}.$$

In particular,

$$T_x(E) = \mathbf{v}_3^\dagger \left(EI - H_{\mathrm{B}}^{(N)}\right)^{-1} \mathbf{v}_9, \tag{6}$$

$$T_y(E) = \mathbf{v}_{12}^\dagger \left(EI - H_{\mathrm{B}}^{(N+2)}\right)^{-1} \mathbf{v}_6. \tag{7}$$

Equations (6) and (7) show that directional anisotropy can arise from two independent sources: the bridge resolvents differ because their segment counts differ, and the frontier-orbital coefficients differ because the attachment sites are not electronically equivalent.

Hypothesis 2 (Rank-one endpoint coupling)**.** *For each $\mu \in \{x, y\}$, suppose that there exist normalized bridge endpoint states*

$$\mathbf{b}_{\mu,L}, \mathbf{b}_{\mu,R} \in \mathcal{H}_{\mathrm{B},\mu},$$

nonzero local hopping parameters $\kappa_{\mu,L}, \kappa_{\mu,R}$, and *attachment-site frontier coefficients c_{p_μ}, c_{q_μ} such that*

$$\mathbf{v}_{p_\mu} = \kappa_{\mu,L} c_{p_\mu} \mathbf{b}_{\mu,L}, \qquad \mathbf{v}_{q_\mu} = \kappa_{\mu,R} c_{q_\mu} \mathbf{b}_{\mu,R}.$$

Define the endpoint-to-endpoint bridge Green's-function element by

$$g_\mu(E) := \left\langle \mathbf{b}_{\mu,L}, G_{\mathrm{B},\mu}(E) \mathbf{b}_{\mu,R} \right\rangle. \tag{8}$$

Lemma 3 (Endpoint factorization)**.** *Under Hypothesis 2,*

$$T_\mu(E) = \overline{\kappa_{\mu,L}}\, \kappa_{\mu,R}\, \overline{c_{p_\mu}}\, c_{q_\mu}\, g_\mu(E).$$

Consequently,

$$|T_\mu(E)| = |\kappa_{\mu,L}\kappa_{\mu,R}|\, |c_{p_\mu} c_{q_\mu}|\, |g_\mu(E)|.$$

Proof. Substitution of the endpoint representations from Hypothesis 2 into Definition 9 gives

$$\begin{aligned} T_\mu(E) &= \left(\kappa_{\mu,L} c_{p_\mu} \mathbf{b}_{\mu,L}\right)^\dagger G_{\mathrm{B},\mu}(E) \left(\kappa_{\mu,R} c_{q_\mu} \mathbf{b}_{\mu,R}\right) \\ &= \overline{\kappa_{\mu,L}}\, \kappa_{\mu,R}\, \overline{c_{p_\mu}}\, c_{q_\mu}\, g_\mu(E). \end{aligned}$$

Taking absolute values proves the second identity. □

Proposition 4 (Nonvanishing directional-coupling criterion)**.** *Fix $\mu \in \{x, y\}$ and suppose that*

$$E \notin \mathrm{Spec}(H_{\mathrm{B},\mu}).$$

Under Hypothesis 2,

$$T_\mu(E) \neq 0$$

if and only if

$$c_{p_\mu} \neq 0, \qquad c_{q_\mu} \neq 0, \qquad g_\mu(E) \neq 0.$$

Proof. The local hopping parameters are nonzero by Hypothesis 2. The conclusion therefore follows immediately from the factorization in Lemma 3. □

Corollary 2 (Two-direction electronic connectivity)**.** *At an energy E belonging to the resolvent sets of both bridge Hamiltonians,*

$$T_x(E) T_y(E) \neq 0$$

if and only if

$$c_3 c_9 c_{12} c_6 \neq 0, \qquad g_x(E) g_y(E) \neq 0.$$

Thus, nonzero frontier-state amplitudes at all four attachment sites and nonzero transmission through both finite bridges are sufficient for electronic connectivity in both lattice directions.

Lemma 5 (Uniform coupling bound on an energy interval)**.** *Let $\mathcal{I} \subset \mathbb{R}$ be compact and suppose that*

$$\mathcal{I} \cap \mathrm{Spec}(H_{\mathrm{B},\mu}) = \varnothing, \qquad g_\mu(E) \neq 0 \quad \text{for every } E \in \mathcal{I}.$$

Then there exists

$$\underline{g}_\mu(\mathcal{I}) > 0$$

such that

$$|g_\mu(E)| \geq \underline{g}_\mu(\mathcal{I}) \qquad \text{for every } E \in \mathcal{I}.$$

Consequently,

$$|T_\mu(E)| \geq |\kappa_{\mu,L}\kappa_{\mu,R}|\, |c_{p_\mu} c_{q_\mu}|\, \underline{g}_\mu(\mathcal{I}).$$

Proof. The resolvent and hence g_μ are continuous on $\mathcal{I}$. Since $|g_\mu|$ is strictly positive on the compact set $\mathcal{I}$, it attains a strictly positive minimum there. The coupling bound then follows from Lemma 3. □

For comparison with the DBC benchmark, let $T_{\mathfrak{R}}(E) \neq 0$ denote its reduced nearest-neighbor coupling and define

$$\Gamma_x(E) := \frac{|T_x(E)|}{|T_{\mathfrak{R}}(E)|}, \qquad \Gamma_y(E) := \frac{|T_y(E)|}{|T_{\mathfrak{R}}(E)|}.$$

The present feasibility analysis requires only

$$\Gamma_x(E) > 0, \qquad \Gamma_y(E) > 0;$$

it does not require either ratio to equal or exceed unity.

Remark 4 (Bridge-length attenuation)**.** *For an off-resonant conjugated bridge, a useful empirical model is*

$$|g^{(m)}(E)| \simeq g_0(E) e^{-\beta(E) m}, \qquad \beta(E) \geq 0.$$

If this approximation is validated over the relevant energy interval, then

$$\frac{|T_y(E)|}{|T_x(E)|} \simeq \frac{|\kappa_{y,L}\kappa_{y,R} c_{12} c_6|}{|\kappa_{x,L}\kappa_{x,R} c_3 c_9|} e^{-2\beta(E)}.$$

This relation predicts directional attenuation caused by the two additional bridge segments. It is not imposed as a universal law: resonances, destructive interference, and attachment-site orbital nodes must be evaluated explicitly.

Remark 5 (Logical limitation)**.** *The condition*

$$T_x(E)T_y(E) \neq 0$$

establishes neither a macroscopic conductivity nor a hydrogen-evolution rate. It excludes only an electronically disconnected direction in the reduced node–bridge model. Charge separation, carrier survival, catalyst access, and proton-reduction energetics remain independent conditions.

5 Rectangular Bloch Spectrum and Two-Dimensional Transport

The Green's-function couplings derived in Section 4 depend in general on the energy parameter E. To obtain a linear Bloch Hamiltonian, fix a comparison energy

$$E_* \notin \mathrm{Spec}(H_{\mathrm{B},x}) \cup \mathrm{Spec}(H_{\mathrm{B},y})$$

and define

$$t_x := T_x(E_*), \qquad t_y := T_y(E_*).$$

The quantities t_x and t_y are treated as frozen effective nearest-neighbor couplings over the spectral window considered below.

Hypothesis 3 (Real nearest-neighbor reduction)**.** *The reduced in-plane Hamiltonian contains one effective frontier state per chrysene node, a common on-site energy $\varepsilon_{\mathfrak{R}}$, and nearest-neighbor couplings t_x and t_y. In the absence of an imposed magnetic flux, phases are chosen so that*

$$t_x, t_y \in \mathbb{R}.$$

Longer-range hopping, disorder, electron–phonon coupling, and interlayer hopping are excluded from the present reduction.

Definition 10 (Rectangular tight-binding Hamiltonian)**.** *Let*

$$\mathcal{H}_{\mathfrak{R}} := \ell^2(\mathbb{Z}^2).$$

For $\psi \in \mathcal{H}_{\mathfrak{R}}$, define

$$\begin{aligned}(H_{\mathfrak{R}}\psi)_{i,j} := \varepsilon_{\mathfrak{R}}\psi_{i,j} &+ t_x\big(\psi_{i+1,j} + \psi_{i-1,j}\big) \\ &+ t_y\big(\psi_{i,j+1} + \psi_{i,j-1}\big).\end{aligned} \tag{9}$$

The first Brillouin zone is

$$\mathcal{B}_{\mathfrak{R}} = \left[-\frac{\pi}{a_N}, \frac{\pi}{a_N}\right) \times \left[-\frac{\pi}{b_{N+2}}, \frac{\pi}{b_{N+2}}\right).$$

For $\mathbf{k} = (k_x, k_y) \in \mathcal{B}_{\mathfrak{R}}$, introduce the Bloch state

$$\psi^{(\mathbf{k})}_{i,j} = e^{\mathrm{i}(k_x i a_N + k_y j b_{N+2})}.$$

Proposition 6 (Rectangular Bloch dispersion)**.** *Under Hypothesis 3, the Bloch energy of $\mathfrak{R}_N$ is*

$$\boxed{E_{\mathfrak{R}}(\mathbf{k}) = \varepsilon_{\mathfrak{R}} + 2t_x \cos(k_x a_N) + 2t_y \cos\big(k_y b_{N+2}\big)}.$$

Proof. Substitution of $\psi^{(\mathbf{k})}$ into (9) gives

$$\psi^{(\mathbf{k})}_{i\pm1,j} = e^{\pm \mathrm{i} k_x a_N}\psi^{(\mathbf{k})}_{i,j},$$

and

$$\psi^{(\mathbf{k})}_{i,j\pm1} = e^{\pm \mathrm{i} k_y b_{N+2}}\psi^{(\mathbf{k})}_{i,j}.$$

Using

$$e^{\mathrm{i}\theta} + e^{-\mathrm{i}\theta} = 2\cos\theta$$

yields (6). □

Theorem 7 (Rectangular spectral width)**.** *The spectral width of $H_{\mathfrak{R}}$ is*

$$\boxed{W_{\mathfrak{R}} = 4\big(|t_x| + |t_y|\big)}.$$

In particular,

$$W_{\mathfrak{R}} > 0$$

if at least one directional coupling is nonzero.

Proof. The variables

$$\cos(k_x a_N) \quad \text{and} \quad \cos\big(k_y b_{N+2}\big)$$

vary independently over $[-1, 1]$. Hence,

$$E_{\max} = \varepsilon_{\mathfrak{R}} + 2|t_x| + 2|t_y|$$

and

$$E_{\min} = \varepsilon_{\mathfrak{R}} - 2|t_x| - 2|t_y|.$$

Their difference gives (7). □

Definition 11 (Band-transport admissibility)**.** *The reduced rectangular model is said to be* kinematically transport-admissible in two dimensions *at E_* if*

$$t_x t_y \neq 0.$$

This definition asserts dispersion in both crystallographic directions; it does not assert a nonzero macroscopic conductivity.

Theorem 8 (Nonzero directional group velocities)**.** *The Bloch group velocities are*

$$v_x(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial E_{\mathfrak{R}}}{\partial k_x} = -\frac{2t_x a_N}{\hbar}\sin(k_x a_N), \tag{10}$$

$$v_y(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial E_{\mathfrak{R}}}{\partial k_y} = -\frac{2t_y b_{N+2}}{\hbar}\sin\big(k_y b_{N+2}\big). \tag{11}$$

If $t_x t_y \neq 0$, then there exists a nonempty open subset $\mathcal{O} \subset \mathcal{B}_{\mathfrak{R}}$ on which

$$v_x(\mathbf{k})v_y(\mathbf{k}) \neq 0.$$

Proof. Equations (10) and (11) follow by differentiation of (6). If $t_x t_y \neq 0$, both velocities are nonzero whenever

$$k_x a_N \notin \pi\mathbb{Z}, \qquad k_y b_{N+2} \notin \pi\mathbb{Z}.$$

The complement of these nodal lines is open and nonempty. □

Corollary 3 (Maximum band velocities)**.** *The maximum velocity magnitudes allowed by the reduced band are*

$$v_{x,\max} = \frac{2|t_x|a_N}{\hbar}, \qquad v_{y,\max} = \frac{2|t_y|b_{N+2}}{\hbar}.$$

Thus, the longer crystallographic period does not alone determine the slower transport direction; both lattice spacing and electronic coupling enter the velocity scale.

Proposition 9 (Directional effective masses)**.** *At a nondegenerate band extremum, the effective masses in the principal directions satisfy*

$$\boxed{m_x^* = \frac{\hbar^2}{2|t_x|a_N^2}, \qquad m_y^* = \frac{\hbar^2}{2|t_y|b_{N+2}^2}}.$$

Proof. Expand the cosine functions in (6) to second order about a band extremum. The quadratic terms have magnitudes

$$|t_x|a_N^2(\delta k_x)^2 \quad \text{and} \quad |t_y|b_{N+2}^2(\delta k_y)^2.$$

Comparison with

$$\frac{\hbar^2(\delta k_\mu)^2}{2m_\mu^*}$$

gives (9). □

Definition 12 (Coupling bottleneck and anisotropy)**.** *Define*

$$t_{\min} := \min\{|t_x|, |t_y|\}, \qquad t_{\max} := \max\{|t_x|, |t_y|\}.$$

When $t_{\min} > 0$, define the coupling-anisotropy ratio

$$\mathcal{A}_t := \frac{t_{\max}}{t_{\min}} \geq 1.$$

A quantitative two-dimensional transport requirement may be written as

$$t_{\min} \geq t_{\text{crit}} > 0,$$

where t_{crit} is fixed independently by a required transfer time, diffusion length, or experimental conductivity.

For comparison with the scalar nearest-neighbor model of the DBC kagome benchmark, let

$$W_{\mathfrak{K}} = 6|t_{\mathfrak{K}}|.$$

With

$$\Gamma_x = \frac{|t_x|}{|t_{\mathfrak{K}}|}, \qquad \Gamma_y = \frac{|t_y|}{|t_{\mathfrak{K}}|},$$

one obtains

$$\frac{W_{\mathfrak{R}}}{W_{\mathfrak{K}}} = \frac{2}{3}\big(\Gamma_x + \Gamma_y\big).$$

The feasibility analysis requires only

$$\Gamma_x > 0, \qquad \Gamma_y > 0,$$

together with the independently selected bottleneck condition (12); it does not require $W_{\mathfrak{R}} \geq W_{\mathfrak{K}}$.

Corollary 4 (Square and one-dimensional limits)**.** *If*

$$a_N = b_{N+2} = d_{\mathfrak{R}}, \qquad t_x = t_y = t_{\mathfrak{R}},$$

then

$$E_{\mathfrak{R}}(\mathbf{k}) = \varepsilon_{\mathfrak{R}} + 2t_{\mathfrak{R}}\big[\cos(k_x d_{\mathfrak{R}}) + \cos\big(k_y d_{\mathfrak{R}}\big)\big],$$

and

$$W_{\mathfrak{R}} = 8|t_{\mathfrak{R}}|.$$

If exactly one of t_x, t_y vanishes, the reduced model becomes dispersive in only one direction and fails Definition 11.

Remark 6 (Transport limitation)**.** *Nonzero group velocity and finite effective mass are kinematic properties of the ideal periodic Hamiltonian. Actual charge delivery also depends on scattering, disorder, localization, excited-state lifetime, recombination, interlayer transfer, and catalyst placement. The diffusion-length conditions introduced below therefore remain independent of the Bloch-spectrum results established in this section.*

6 Optical and Charge-Separation Feasibility

Electronic dispersion can contribute to photocatalysis only if incident radiation populates an electronically active state and that excitation can form a charge-separated state before local relaxation occurs. The optical and charge-separation requirements are therefore imposed independently of the Bloch-spectrum conditions in Section 5.

Definition 13 (Optically accessible state)**.** *Let*

$$|\Psi_0\rangle \quad \text{and} \quad |\Psi_1\rangle$$

denote, respectively, the electronic ground state and a candidate excited state of $\mathfrak{R}_N$*. The corresponding transition dipole is*

$$\boldsymbol{\mu}_{01} := \langle\Psi_0|\widehat{\boldsymbol{\mu}}|\Psi_1\rangle .$$

The state $|\Psi_1\rangle$ *is called* optically accessible *if*

$$\|\boldsymbol{\mu}_{01}\|^2 > 0$$

and its excitation energy lies within the incident spectral window.

Let $\Phi_\gamma(\lambda)$ denote the incident spectral photon flux, with units

$$\text{photons}\,\text{m}^{-2}\,\text{s}^{-1}\,\text{nm}^{-1},$$

and let $\alpha_{\mathfrak{R}}(\lambda)$ be the effective absorption coefficient of the candidate. For illuminated area $A_{\text{ill}} > 0$, effective optical path length $L > 0$, and Avogadro constant N_{A}, define the molar absorbed-photon rate by

$$\dot{n}_{\text{abs},\mathfrak{R}} := \frac{A_{\text{ill}}}{N_{\text{A}}} \int_{\lambda_1}^{\lambda_2} \Phi_\gamma(\lambda) \left[1 - e^{-\alpha_{\mathfrak{R}}(\lambda)L}\right] d\lambda. \tag{12}$$

Definition 14 (Optical feasibility)**.** *The candidate is* optically feasible *under the prescribed illumination if there exists*

$$\underline{\dot{n}}_{\text{abs}} > 0$$

such that

$$\dot{n}_{\text{abs},\mathfrak{R}} \geq \underline{\dot{n}}_{\text{abs}}.$$

The lower bound is to be determined from calibrated absorption measurements or a validated electronic-structure calculation, rather than inferred from the presence of the chrysene chromophore alone.

Proposition 10 (Sufficient condition for positive absorption)**.** *Suppose that there exists a measurable set*

$$\mathcal{L} \subseteq [\lambda_1, \lambda_2]$$

of positive measure such that

$$\Phi_\gamma(\lambda) > 0, \qquad \alpha_{\mathfrak{R}}(\lambda) > 0$$

for every $\lambda \in \mathcal{L}$*. Then*

$$\dot{n}_{\text{abs},\mathfrak{R}} > 0.$$

Proof. For $L > 0$ and $\lambda \in \mathcal{L}$,

$$1 - e^{-\alpha_{\mathfrak{R}}(\lambda)L} > 0.$$

The integrand in (12) is therefore nonnegative everywhere and strictly positive on a set of positive measure. Its integral is consequently strictly positive. □

Optical excitation does not itself imply useful charge separation. To state the thermodynamic requirement, let $|D^*A\rangle$ denote an optically prepared state and let $|D^+A^-\rangle$ denote an effective charge-separated state. The labels D and A may represent node-dominated, bridge-dominated, adjacent-node, interlayer, or metal-conditioned electronic states; they need not correspond to separate molecular species.

Definition 15 (Charge-separation free energy)**.** *The exact charge-separation free-energy change is*

$$\Delta G_{\text{CS}} := G(D^+A^-) - G(D^*A).$$

Under a Rehm–Weller-type electrochemical approximation, it is written as

$$\Delta G_{\text{CS}} = F\left(E_{\text{ox}}^{D} - E_{\text{red}}^{A}\right) - E_{00} - J_{\text{CS}}, \tag{13}$$

where F *is the Faraday constant,* E_{ox}^{D} *is the donor oxidation potential,* E_{red}^{A} *is the acceptor reduction potential,* E_{00} *is the molar zero–zero excitation energy, and* $J_{\text{CS}} \geq 0$ *denotes Coulombic stabilization of the charge-separated state. All potentials and free energies are to be reported under a common solvent, pH, temperature, and reference-electrode convention.*

Definition 16 (Thermodynamic charge-separation margin)**.** *For a prescribed margin* $\delta_{\text{CS}} > 0$*, the candidate is* thermodynamically admissible for charge separation *if*

$$\boxed{\Delta G_{\text{CS}} \leq -\delta_{\text{CS}} < 0}.$$

The strict margin in (16) distinguishes a robustly favorable prediction from an equality that may change sign under experimental or computational uncertainty.

Proposition 11 (Uncertainty-robust charge-separation criterion)**.** *Suppose that a prediction $\widehat{\Delta G}_{\mathrm{CS}}$ satisfies*

$$\left|\Delta G_{\mathrm{CS}} - \widehat{\Delta G}_{\mathrm{CS}}\right| \le \epsilon_{\mathrm{CS}},$$

where $\epsilon_{\mathrm{CS}} \ge 0$ is a calibrated uncertainty bound. If

$$\widehat{\Delta G}_{\mathrm{CS}} + \epsilon_{\mathrm{CS}} \le -\delta_{\mathrm{CS}},$$

then

$$\Delta G_{\mathrm{CS}} \le -\delta_{\mathrm{CS}}.$$

Proof. The uncertainty bound gives

$$\Delta G_{\mathrm{CS}} \le \widehat{\Delta G}_{\mathrm{CS}} + \epsilon_{\mathrm{CS}}.$$

Application of (11) yields the conclusion. □

Thermodynamic admissibility must be accompanied by a finite charge-separation rate. Let V_{DA} denote the electronic coupling between the optically prepared and charge-separated states, and let $\lambda_{\mathrm{CS}} > 0$ denote the corresponding reorganization energy. In the nonadiabatic Marcus approximation,

$$k_{\mathrm{CS}} = \frac{2\pi}{\hbar}|V_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{CS}} k_{\mathrm{B}} T}} \exp\left[-\frac{(\Delta G_{\mathrm{CS}} + \lambda_{\mathrm{CS}})^2}{4\lambda_{\mathrm{CS}} k_{\mathrm{B}} T}\right]. \quad (14)$$

Lemma 12 (Positive charge-separation rate)**.** *If*

$$T > 0, \qquad \lambda_{\mathrm{CS}} > 0, \qquad |V_{\mathrm{DA}}| > 0,$$

and ΔG_{CS} is finite, then

$$k_{\mathrm{CS}} > 0.$$

Proof. Every factor on the right-hand side of (14) is finite and strictly positive under the stated hypotheses. □

Let k_{loss} denote the combined first-order rate of radiative decay, internal conversion, nonproductive trapping, and other losses from the initially excited state. The charge-separation branching yield is

$$\Phi_{\mathrm{CS}} := \frac{k_{\mathrm{CS}}}{k_{\mathrm{CS}} + k_{\mathrm{loss}}}. \quad (15)$$

Definition 17 (Optical–charge-separation feasibility)**.** *For prescribed constants*

$$\underline{\dot n}_{\mathrm{abs}} > 0, \qquad \delta_{\mathrm{CS}} > 0, \qquad \phi_{\mathrm{CS,min}} \in (0,1),$$

the candidate $\mathfrak{R}_N$ is optically and charge-separation feasible *if*

$$\dot n_{\mathrm{abs},\mathfrak{R}} \ge \underline{\dot n}_{\mathrm{abs}},$$
$$\Delta G_{\mathrm{CS}} \le -\delta_{\mathrm{CS}},$$

and

$$\Phi_{\mathrm{CS}} \ge \phi_{\mathrm{CS,min}}.$$

Equivalently, (17) holds if and only if

$$k_{\mathrm{CS}} \ge \frac{\phi_{\mathrm{CS,min}}}{1 - \phi_{\mathrm{CS,min}}} k_{\mathrm{loss}}.$$

Remark 7 (Relation to the DBC benchmark)**.** *The DBC experiment supplies precedent that a planar, chrysene-related, conjugated framework can satisfy the sequence*

$$\text{photon absorption} \longrightarrow \text{excited-state formation} \longrightarrow \text{charge separation}.$$

For $\mathfrak{R}_N$, however, the transition dipole, ΔG_{CS}, V_{DA}, λ_{CS}, and k_{loss} remain candidate-specific quantities. The conditions in this section must therefore be evaluated prospectively and are not inherited from $\mathfrak{R}$.

7 Electron Delivery and Hydrogen-Reduction Conditions

A charge-separated state is useful for hydrogen evolution only if its electron survives long enough to reach an accessible platinum site and retains sufficient reducing free energy after transport and interfacial injection. These requirements are imposed separately from optical absorption and initial charge separation.

Definition 18 (Charge-separated-state lifetime)**.** *Let $k_{\mathrm{CR}} > 0$ denote the effective first-order rate of geminate recombination, nongeminate recombination, and irreversible trapping of the electron-bearing charge-separated state. Its effective lifetime is*

$$\tau_{\mathrm{CS}} := \frac{1}{k_{\mathrm{CR}}}.$$

At length scales exceeding the primitive cell, let $n(x,y,t)$ denote the coarse-grained density of surviving electron-bearing states. In the principal crystallographic coordinates, the anisotropic diffusion–recombination model is

$$\frac{\partial n}{\partial t} = D_x \frac{\partial^2 n}{\partial x^2} + D_y \frac{\partial^2 n}{\partial y^2} - k_{\mathrm{CR}} n, \quad (16)$$

where

$$D_x > 0, \qquad D_y > 0$$

are effective directional diffusion coefficients.

Definition 19 (Directional diffusion lengths)**.** *The characteristic electron-survival lengths are*

$$L_x := \sqrt{D_x \tau_{\mathrm{CS}}} = \sqrt{\frac{D_x}{k_{\mathrm{CR}}}}, \qquad L_y := \sqrt{D_y \tau_{\mathrm{CS}}} = \sqrt{\frac{D_y}{k_{\mathrm{CR}}}}.$$

Let

$$\boldsymbol{\ell}_{\mathrm{Pt}} = (\ell_{\mathrm{Pt},x}, \ell_{\mathrm{Pt},y})$$

denote the displacement from the location at which the charge-separated state is formed to a catalytically accessible platinum site.

Definition 20 (Anisotropic catalyst-access parameter)**.** *Define*

$$\chi_{\mathrm{Pt}}^2 := \frac{\ell_{\mathrm{Pt},x}^2}{L_x^2} + \frac{\ell_{\mathrm{Pt},y}^2}{L_y^2}.$$

The platinum site is called diffusion-accessible within one charge-separated-state lifetime *if*

$$\boxed{\chi_{\mathrm{Pt}} \le 1}.$$

For a predominantly directional path, the sufficient condition (20) reduces to

$$\ell_{\mathrm{Pt},\mu} \le L_\mu \qquad \text{for some } \mu \in \{x, y\}.$$

Thus, a large total bandwidth cannot compensate for a vanishing diffusion length along the path connecting the excitation site to the catalyst.

Remark 8 (Relation to the Bloch model)**.** *The Bloch velocities and effective masses derived in Section 5 constrain the possible values of D_x and D_y, but do not determine them without a scattering, localization, and disorder model. The diffusion coefficients must therefore be obtained from a validated transport calculation, time-resolved spectroscopy, conductivity measurement, or calibrated kinetic fit.*

Let $k_{\mathrm{tr}} > 0$ denote an effective rate of electron arrival at a catalyst-accessible region. Competition between transport and recombination gives the survival factor

$$\Phi_{\mathrm{tr}} := \frac{k_{\mathrm{tr}}}{k_{\mathrm{tr}} + k_{\mathrm{CR}}}. \tag{17}$$

Proposition 13 (Transport-survival threshold)**.** *For a prescribed*

$$\phi_{\mathrm{tr,min}} \in (0, 1),$$

the condition

$$\Phi_{\mathrm{tr}} \ge \phi_{\mathrm{tr,min}}$$

holds if and only if

$$\boxed{k_{\mathrm{tr}} \ge \frac{\phi_{\mathrm{tr,min}}}{1 - \phi_{\mathrm{tr,min}}} k_{\mathrm{CR}}}.$$

Proof. Starting from

$$\frac{k_{\mathrm{tr}}}{k_{\mathrm{tr}} + k_{\mathrm{CR}}} \ge \phi_{\mathrm{tr,min}},$$

multiplication by the positive denominator and rearrangement give (13). Each algebraic step is reversible. □

Arrival near platinum must be followed by interfacial electron injection. Let $k_{\mathrm{inj}} > 0$ denote the forward injection rate and let $k_{\mathrm{back}} \ge 0$ denote back-electron transfer from the interfacial state.

Definition 21 (Platinum-injection yield)**.** *The interfacial injection yield is*

$$\Phi_{\mathrm{inj}} := \frac{k_{\mathrm{inj}}}{k_{\mathrm{inj}} + k_{\mathrm{back}}}.$$

For a prescribed $\phi_{\mathrm{inj,min}} \in (0, 1)$, the injection requirement is

$$\Phi_{\mathrm{inj}} \ge \phi_{\mathrm{inj,min}},$$

or, equivalently,

$$k_{\mathrm{inj}} \ge \frac{\phi_{\mathrm{inj,min}}}{1 - \phi_{\mathrm{inj,min}}} k_{\mathrm{back}}.$$

It remains to require that the transported electron can reduce protons under the specified electrochemical boundary condition. Let

$$E_{\mathfrak{R}/\mathfrak{R}^-}$$

denote the reduction potential of the electron-bearing state relative to a stated reference electrode. Under hydrogen pressure p_{H_2}, the Nernst potential of the $\mathrm{H}^+/\mathrm{H}_2$ couple is

$$E_{\mathrm{H}^+/\mathrm{H}_2} = E^\circ_{\mathrm{H}^+/\mathrm{H}_2} - \frac{RT}{F} \ln(10)\,\mathrm{pH} - \frac{RT}{2F} \ln p_{\mathrm{H}_2}. \tag{18}$$

Definition 22 (Effective hydrogen-reduction free energy)**.** *Let $\eta_{\mathrm{req}} \ge 0$ denote the combined interfacial and kinetic overpotential required under the declared platinum loading and reaction conditions. The effective free-energy change per mole of transferred electrons is*

$$\Delta G_{\mathrm{H}} := -F \left[E_{\mathrm{H}^+/\mathrm{H}_2} - E_{\mathfrak{R}/\mathfrak{R}^-} - \eta_{\mathrm{req}} \right]. \tag{19}$$

For a prescribed margin $\delta_{\mathrm{H}} > 0$, the electron-bearing state *is* thermodynamically admissible for hydrogen reduction *if*

$$\boxed{\Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}} < 0}.$$

Equivalently,

$$E_{\mathrm{H^+/H_2}} - E_{\mathfrak{R}/\mathfrak{R}^-} - \eta_{\mathrm{req}} \geq \frac{\delta_{\mathrm{H}}}{F}.$$

Proposition 14 (Uncertainty-robust hydrogen-reduction criterion)**.** *Suppose that a predicted free energy $\widehat{\Delta G}_{\mathrm{H}}$ satisfies*

$$\left|\Delta G_{\mathrm{H}} - \widehat{\Delta G}_{\mathrm{H}}\right| \leq \epsilon_{\mathrm{H}}.$$

If

$$\widehat{\Delta G}_{\mathrm{H}} + \epsilon_{\mathrm{H}} \leq -\delta_{\mathrm{H}},$$

then

$$\Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}}.$$

Proof. The uncertainty bound implies

$$\Delta G_{\mathrm{H}} \leq \widehat{\Delta G}_{\mathrm{H}} + \epsilon_{\mathrm{H}}.$$

Application of (14) proves the result. □

Definition 23 (Electron-delivery and reduction feasibility)**.** *The candidate $\mathfrak{R}_N$ is* electron-delivery and hydrogen-reduction feasible *under $\mathscr{C}_{\mathrm{HER}}$ if*

$$\chi_{\mathrm{Pt}} \leq 1,$$

$$\Phi_{\mathrm{tr}} \geq \phi_{\mathrm{tr,min}} > 0,$$

$$\Phi_{\mathrm{inj}} \geq \phi_{\mathrm{inj,min}} > 0,$$

and

$$\Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}} < 0.$$

Remark 9 (Role of platinum and the sacrificial donor)**.** *The platinum cocatalyst supplies a kinetically competent terminal site for proton reduction, while ascorbic acid removes photogenerated oxidizing equivalents. These boundary conditions reduce the burden on $\mathfrak{R}_N$, but they do not eliminate the requirements of electron survival, catalyst access, interfacial injection, and favorable reduction energetics. Satisfaction of the conditions above concerns only the hydrogen-evolution half-reaction; it does not establish water oxidation or overall artificial photosynthesis.*

8 Detectable Hydrogen-Evolution Lower Bound

The preceding sections provide separate optical, thermodynamic, transport, and interfacial conditions. We now combine them into a lower bound on the hydrogen-evolution rate. The bound is not obtained from the DBC rate by analogy; it is constructed from independently bounded candidate-specific quantities.

Let $m_{\mathfrak{R}} > 0$ denote the mass of the candidate material in the illuminated sample. Define its mass-normalized absorbed-photon rate by

$$\mathcal{A}_{\mathfrak{R}} := \frac{\dot{n}_{\mathrm{abs},\mathfrak{R}}}{m_{\mathfrak{R}}}, \tag{20}$$

with units

$$\text{mol photons g}^{-1}\,\text{s}^{-1}.$$

Definition 24 (Catalytic electron-utilization efficiency)**.** *Let*

$$\eta_{\mathrm{Pt}} \in [0, 1]$$

denote the fraction of electrons injected into catalyst-accessible platinum states that contribute to persistent reducing equivalents for the formation of molecular hydrogen. Losses incorporated into $1 - \eta_{\mathrm{Pt}}$ include interfacial trapping, unproductive surface reactions, catalyst poisoning, and electron consumption not resulting in H_2.

Hypothesis 4 (Sequential branching and electron accounting)**.** *Each absorbed photon produces at most one electron-bearing excitation entering the modeled sequence. Charge separation, transport, interfacial injection, and catalytic utilization are represented by successive branching efficiencies*

$$\Phi_{\mathrm{CS}}, \qquad \Phi_{\mathrm{tr}}, \qquad \Phi_{\mathrm{inj}}, \qquad \eta_{\mathrm{Pt}}.$$

Two productively delivered electrons are required per molecule of hydrogen.

Under Hypothesis 4, the mass-normalized hydrogen-evolution rate is represented by

$$R_{\mathrm{H_2},\mathfrak{R}} = \frac{1}{2}\mathcal{A}_{\mathfrak{R}}\Phi_{\mathrm{CS}}\Phi_{\mathrm{tr}}\Phi_{\mathrm{inj}}\eta_{\mathrm{Pt}}. \tag{21}$$

The factors in (21) are not treated as arbitrary positive constants. Let experimentally or computationally supported bounds satisfy

$$\mathcal{A}_{\mathfrak{R}} \geq \underline{\mathcal{A}}_{\mathfrak{R}} > 0, \tag{22}$$

$$k_{\mathrm{CS}} \geq \underline{k}_{\mathrm{CS}} > 0, \qquad k_{\mathrm{loss}} \leq \overline{k}_{\mathrm{loss}} < \infty, \tag{23}$$

$$k_{\mathrm{tr}} \geq \underline{k}_{\mathrm{tr}} > 0, \qquad k_{\mathrm{CR}} \leq \overline{k}_{\mathrm{CR}} < \infty, \tag{24}$$

$$k_{\mathrm{inj}} \geq \underline{k}_{\mathrm{inj}} > 0, \qquad k_{\mathrm{back}} \leq \overline{k}_{\mathrm{back}} < \infty, \tag{25}$$

$$\eta_{\mathrm{Pt}} \geq \underline{\eta}_{\mathrm{Pt}} > 0. \tag{26}$$

Lemma 15 (Branching-fraction lower bounds)**.** *Under* (23)–(25)*,*

$$\Phi_{\mathrm{CS}} \geq \underline{\Phi}_{\mathrm{CS}} := \frac{\underline{k}_{\mathrm{CS}}}{\underline{k}_{\mathrm{CS}} + \overline{k}_{\mathrm{loss}}}, \tag{27}$$

$$\Phi_{\mathrm{tr}} \geq \underline{\Phi}_{\mathrm{tr}} := \frac{\underline{k}_{\mathrm{tr}}}{\underline{k}_{\mathrm{tr}} + \overline{k}_{\mathrm{CR}}}, \tag{28}$$

$$\Phi_{\mathrm{inj}} \geq \underline{\Phi}_{\mathrm{inj}} := \frac{\underline{k}_{\mathrm{inj}}}{\underline{k}_{\mathrm{inj}} + \overline{k}_{\mathrm{back}}}. \tag{29}$$

Proof. For $x > 0$ and $y \geq 0$, the function

$$f(x, y) = \frac{x}{x + y}$$

is increasing in x and decreasing in y. Substitution of the corresponding lower bound for the productive rate and upper bound for the competing rate proves each inequality. □

Theorem 16 (Hydrogen-evolution lower bound)**.** *Suppose that the following conditions hold:*

1. *the optical lower bound* (22)*;*
2. *two-direction electronic connectivity,*
$$t_x t_y \neq 0;$$
3. *thermodynamically favorable charge separation,*
$$\Delta G_{\mathrm{CS}} \leq -\delta_{\mathrm{CS}} < 0;$$
4. *catalyst accessibility,*
$$\chi_{\mathrm{Pt}} \leq 1;$$
5. *thermodynamically favorable hydrogen reduction,*
$$\Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}} < 0;$$
6. *the kinetic bounds* (23)–(25)*; and*
7. *the catalytic-utilization bound* (26).

Then

$$R_{\mathrm{H}_2,\mathfrak{R}} \geq R_{\mathfrak{R}}^{\mathrm{LB}} > 0,$$

where

$$\boxed{R_{\mathfrak{R}}^{\mathrm{LB}} := \frac{\underline{\mathcal{A}}_{\mathfrak{R}}}{2} \frac{\underline{k}_{\mathrm{CS}}}{\underline{k}_{\mathrm{CS}} + \overline{k}_{\mathrm{loss}}} \frac{\underline{k}_{\mathrm{tr}}}{\underline{k}_{\mathrm{tr}} + \overline{k}_{\mathrm{CR}}} \times \frac{\underline{k}_{\mathrm{inj}}}{\underline{k}_{\mathrm{inj}} + \overline{k}_{\mathrm{back}}} \underline{\eta}_{\mathrm{Pt}}.} \tag{30}$$

Proof. By Lemma 15, each branching efficiency in (21) is bounded below by the corresponding expression in (27)–(29). The absorption and platinum-utilization factors are bounded below by (22) and (26). Multiplication of these nonnegative inequalities gives (30). Every factor in $R_{\mathfrak{R}}^{\mathrm{LB}}$ is strictly positive, and hence

$$R_{\mathfrak{R}}^{\mathrm{LB}} > 0.$$

The thermodynamic and catalyst-access hypotheses ensure that the productive sequence represented by the kinetic factors is admissible under the declared reaction boundary. □

Definition 25 (Background-corrected experimental signal)**.** *Let*

$$R_{\mathrm{light,mat}}, \qquad R_{\mathrm{dark,mat}}, \qquad R_{\mathrm{light,blank}}$$

denote the measured rates under illuminated material, dark material, and illuminated no-material conditions, respectively. Define

$$R_{\mathrm{net}} := R_{\mathrm{light,mat}} - \max\left\{R_{\mathrm{dark,mat}}, R_{\mathrm{light,blank}}\right\}.$$

All rates are to be evaluated using the same normalization, sampling interval, and gas-analysis procedure.

Corollary 5 (Detectable-activity criterion)**.** *Let* $R_{\mathrm{LOQ}} > 0$ *be the independently determined, background-corrected limit of quantification. Under the hypotheses of Theorem* 16*, if*

$$\boxed{R_{\mathfrak{R}}^{\mathrm{LB}} > R_{\mathrm{LOQ}}},$$

then the model predicts a quantifiable hydrogen-evolution signal under the specified Pt-assisted sacrificial-donor conditions.

For comparison with the DBC benchmark, define the dimensionless detection fraction

$$\varepsilon_{\mathrm{det}} := \frac{R_{\mathrm{LOQ}}}{R_{\mathrm{H}_2,\mathfrak{R}}}.$$

Because $R_{\mathrm{H}_2,\mathfrak{R}} > 0$, condition (5) is equivalent to

$$\frac{R_{\mathfrak{R}}^{\mathrm{LB}}}{R_{\mathrm{H}_2,\mathfrak{R}}} > \varepsilon_{\mathrm{det}}.$$

No condition of the form

$$R_{\mathfrak{R}}^{\mathrm{LB}} \geq R_{\mathrm{H}_2,\mathfrak{R}}$$

is imposed.

Remark 10 (Non-tautological content)**.** *Theorem 16 does not infer activity merely by declaring abstract efficiencies to be positive. Its inputs are bounded quantities tied to absorption measurements, time-resolved kinetic rates, diffusion and catalyst-access estimates, electrochemical free energies, and controlled platinum utilization. The theorem can fail if any required lower bound vanishes, if a thermodynamic margin changes sign, or if the resulting rate lies below* R_{LOQ}.

Remark 11 (Status when a feasibility gate fails)**.** *If one or more hypotheses of Theorem 16 cannot be established, the certified lower bound is assigned the value*

$$R_{\mathfrak{R}}^{\mathrm{LB}} := 0.$$

This convention does not prove that the experimental rate is zero; it states only that the present model supplies no strictly positive certified lower bound.

9 Metal-Conditioned Extension

A metal ion is not required for the unconditioned feasibility analysis, but it may provide a controlled means of modifying orbital energies, charge localization, interlayer geometry, or electron-transfer kinetics. Its effect must be evaluated together with the possibility of excited-state quenching.

Definition 26 (Metal condition)**.** *A metal condition is the tuple*

$$\mathfrak{m} = \left(M, q, S, \mathbf{R}_M, \mathcal{L}, \mathcal{E}\right),$$

where M is the metal identity, q its oxidation state, S its spin state, $\mathbf{R}_M$ its position relative to the chrysene network, $\mathcal{L}$ its ligand or counterion environment, and $\mathcal{E}$ the surrounding dielectric and chemical environment. The corresponding metal-conditioned candidate is denoted by

$$\mathfrak{R}_N^{(\mathfrak{m})}.$$

Let $\mathcal{H}_\pi$ be the reduced chrysene-network space and $\mathcal{H}_M$ the selected metal-centered orbital space. The coupled Hamiltonian is written as

$$H_{\mathfrak{R}}^{(\mathfrak{m})} = \begin{pmatrix} H_{\mathfrak{R}} & V_{\pi M} \\ V_{M\pi} & H_M \end{pmatrix}, \qquad V_{M\pi} = V_{\pi M}^{\dagger}. \tag{31}$$

For

$$E \notin \mathrm{Spec}(H_M),$$

elimination of the metal subspace gives

$$H_{\mathrm{eff}}^{(\mathfrak{m})}(E) = H_{\mathfrak{R}} + \Sigma_M(E), \qquad \Sigma_M(E) := V_{\pi M}(EI - H_M)^{-1} V_{M\pi}. \tag{32}$$

Proposition 17 (Bounded metal perturbation)**.** *At fixed E, every eigenvalue of $H_{\mathrm{eff}}^{(\mathfrak{m})}(E)$ differs from the corresponding eigenvalue of $H_{\mathfrak{R}}$ by no more than*

$$\|\Sigma_M(E)\|.$$

Proof. The assertion follows from the standard eigenvalue perturbation bound for Hermitian matrices applied to

$$H_{\mathrm{eff}}^{(\mathfrak{m})}(E) = H_{\mathfrak{R}} + \Sigma_M(E).$$

□

The conditioned charge-separation and hydrogen-reduction free energies are denoted by

$$\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} \quad \text{and} \quad \Delta G_{\mathrm{H}}^{(\mathfrak{m})}.$$

Corollary 6 (Preservation of thermodynamic feasibility)**.** *Suppose that*

$$\Delta G_{\mathrm{CS}} \leq -\delta_{\mathrm{CS}}, \qquad \Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}},$$

and that the metal-induced changes satisfy

$$\left|\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} - \Delta G_{\mathrm{CS}}\right| \leq \zeta_{\mathrm{CS}} < \delta_{\mathrm{CS}},$$

$$\left|\Delta G_{\mathrm{H}}^{(\mathfrak{m})} - \Delta G_{\mathrm{H}}\right| \leq \zeta_{\mathrm{H}} < \delta_{\mathrm{H}}.$$

Then

$$\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} \leq -(\delta_{\mathrm{CS}} - \zeta_{\mathrm{CS}}) < 0,$$

and

$$\Delta G_{\mathrm{H}}^{(\mathfrak{m})} \leq -(\delta_{\mathrm{H}} - \zeta_{\mathrm{H}}) < 0.$$

For a metal intended to improve an otherwise unfavorable alignment, the conditioned quantities must instead be shown directly to satisfy

$$\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} \leq -\delta_{\mathrm{CS}}^{(\mathfrak{m})} < 0, \qquad \Delta G_{\mathrm{H}}^{(\mathfrak{m})} \leq -\delta_{\mathrm{H}}^{(\mathfrak{m})} < 0.$$

Energetic improvement is insufficient if the metal introduces a rapid nonradiative decay channel. Accordingly, the additional kinetic requirement is

$$\tau_{\mathrm{CS}}^{(\mathfrak{m})} \geq \tau_{\mathrm{tr}}^{(\mathfrak{m})}, \tag{33}$$

or equivalently,

$$k_{\mathrm{tr}}^{(\mathfrak{m})} \geq k_{\mathrm{CR}}^{(\mathfrak{m})}.$$

Remark 12 (Distinct metal roles)**.** *Mg may be treated initially as a comparatively redox-inert electrostatic and structural conditioner; it is not assumed to be a hydrogen-evolution catalyst. Redox-active ions such as Fe, Co, or Ni may introduce electron-relay or catalytic states, but may also increase spin-mediated or metal-centered nonradiative relaxation. Oxidation state, spin state, metal–π distance, counterions, and environment must therefore be specified for every calculation and measurement. Platinum remains the terminal hydrogen-evolution cocatalyst unless an alternative catalytic function is established independently.*

The metal-conditioned system is certified as detectable only if all hypotheses of Theorem 16, evaluated with the conditioned parameters, yield

$$R_{\mathfrak{R}}^{(\mathfrak{m}),\mathrm{LB}} > R_{\mathrm{LOQ}}.$$

Thus, metal incorporation expands the design space but does not replace the optical, thermodynamic, kinetic, or catalyst-access requirements.

10 Falsifiability and Phase I Tests

The analytical framework is falsifiable only if its parameters, uncertainty margins, and decision thresholds are fixed before the prospective hydrogen-evolution measurements. Failure of a required condition must be permitted to reject either an individual candidate or the reduced model used to select it.

Definition 27 (Prospective candidate set)**.** *Let*

$$\mathscr{P} = \left\{\mathfrak{R}_N^{(1)}, \ldots, \mathfrak{R}_N^{(5)}\right\}$$

denote five candidate structures selected before experimental characterization. For each candidate, the predicted geometry, absorption spectrum, directional couplings, redox potentials, uncertainty intervals, and hydrogen-evolution lower bound shall be recorded before the corresponding prospective measurements are unblinded.

The following quantities shall likewise be specified before hydrogen-evolution testing:

$$t_{\mathrm{crit}}, \quad \delta_{\mathrm{CS}}, \quad \delta_{\mathrm{H}}, \quad \phi_{\mathrm{CS,min}}, \quad \phi_{\mathrm{tr,min}}, \quad \phi_{\mathrm{inj,min}}, \quad R_{\mathrm{LOQ}}.$$

The limit R_{LOQ} shall be established from instrument calibration, blank measurements, sample mass, gas volume, and the declared sampling interval rather than inferred from the observed candidate results.

Definition 28 (Candidate-level success)**.** *For candidate $q \in \{1, \ldots, 5\}$, let*

$$\underline{R}_{\mathrm{net},q}^{(1-\alpha)}$$

denote a one-sided $(1-\alpha)$-level lower confidence bound on its background-corrected hydrogen-evolution rate, using a confidence level and replicate plan fixed before testing. Candidate q satisfies the prospective detectability criterion if

$$\boxed{\underline{R}_{\mathrm{net},q}^{(1-\alpha)} > R_{\mathrm{LOQ}}}.$$

Definition 29 (Phase I feasibility success)**.** *The Phase I feasibility demonstration succeeds if there exists at least one prospectively selected candidate satisfying*

$$\exists q \in \{1, \ldots, 5\} \quad \text{such that} \quad \underline{R}_{\mathrm{net},q}^{(1-\alpha)} > R_{\mathrm{LOQ}},$$

and the signal is absent or significantly smaller under the dark, no-material, and no-Pt controls. The candidate is not required to equal or exceed the DBC hydrogen-evolution rate.

Where a DBC material or another validated photocatalytic standard is available, it may be included as a positive assay control under the same illumination, donor, platinum, sampling, and gas-analysis conditions. Its purpose is to verify that the experimental system can detect photocatalytic hydrogen evolution; its rate is not used as the acceptance threshold for $\mathfrak{R}_N$.

Proposition 18 (Prospective rejection rule)**.** *A candidate cannot be certified by Theorem 16 if any of the following occurs:*

$$t_{\min} < t_{\mathrm{crit}},$$

$$\Delta G_{\mathrm{CS}} + \epsilon_{\mathrm{CS}} > -\delta_{\mathrm{CS}},$$

$$\chi_{\mathrm{Pt}} > 1,$$

$$\Delta G_{\mathrm{H}} + \epsilon_{\mathrm{H}} > -\delta_{\mathrm{H}},$$

or

$$R_{\mathfrak{R}}^{\mathrm{LB}} \leq R_{\mathrm{LOQ}}.$$

Proof. Each listed inequality contradicts a required hypothesis of Theorem 16 or Corollary 5. The theorem therefore supplies no certified detectable lower bound for that candidate. □

If a metal-conditioned candidate is included, its metal identity, oxidation state, spin state, geometry, counterions, and environ-

Table 1: Prospective tests of the rectangular-network feasibility conditions.

Model claim	Primary determination	Required result	Falsification or failure condition
Periodic rectangular geometry	Periodic geometry optimization; structural characterization if synthesized	Finite $a_N, b_{N+2} > 0$ and preservation of the intended $N/(N+2)$ connectivity	Collapse, bond rearrangement, or persistent topology inconsistent with $\mathfrak{R}_N$
Two-direction coupling	Fragment or periodic electronic-structure calculation of $T_x(E)$ and $T_y(E)$	$t_{\min} = \min\{\lvert T_x(E_*)\rvert, \lvert T_y(E_*)\rvert\} \geq t_{\text{crit}}$	An attachment-site orbital node, bridge antiresonance, or uncertainty interval extending below t_{crit}
Useful optical absorption	Calibrated UV–visible spectroscopy and TD-DFT	$\mathcal{A}_{\mathfrak{R}} \geq \underline{\mathcal{A}}_{\mathfrak{R}} > 0$ over the illumination window	Insufficient spectral overlap or inability to establish a positive absorption lower bound
Charge separation	Matched-condition electrochemistry, E_{00}, and time-resolved spectroscopy	$\Delta G_{\text{CS}} \leq -\delta_{\text{CS}}, \qquad \Phi_{\text{CS}} \geq \phi_{\text{CS,min}}$	Unfavorable worst-case free energy or charge separation slower than the predeclared loss threshold
Electron delivery	Transient spectroscopy, photoconductivity, transport calculation, and catalyst-distance estimate	$\chi_{\text{Pt}} \leq 1, \qquad \Phi_{\text{tr}} \geq \phi_{\text{tr,min}}$	Recombination before catalyst access or failure of the directional diffusion-length condition
Hydrogen-reduction alignment	Electrochemical potential referenced to the H^+/H_2 couple	$\Delta G_{\text{H}} \leq -\delta_{\text{H}}$ after uncertainty and overpotential	Worst-case reduction free energy nonnegative or insufficient energetic margin
Hydrogen evolution	Gas chromatography under illuminated, dark, no-material, and no-Pt controls	Background-corrected lower confidence bound greater than R_{LOQ}	No statistically and analytically quantifiable separation from the controls

ment shall be fixed before testing. It must satisfy the same optical, thermodynamic, kinetic, catalyst-access, control, and detectability criteria as the unconditioned material. Metal incorporation is not treated as a post hoc explanation for an unsuccessful result.

> **Remark 13** (Meaning of a negative result)**.** *Failure of all five candidates would reject the proposed Phase I feasibility claim under the tested structures and boundary conditions. It would not prove that every* $3, 6, 9, 12$*-connected chrysene material is inactive. The failed inequalities would instead identify whether the limiting cause was structural realization, optical absorption, directional coupling, charge separation, transport, energetic alignment, catalyst access, or the hydrogen-evolution assay itself.*

11 Discussion, Limitations, and Conclusion

11.1 Interpretation relative to the DBC benchmark

The DBC-sp^2c-COF establishes that a planar, conjugated, dibenzochrysene-based framework can absorb visible light, generate and separate charge, transport reducing equivalents, and support Pt-assisted hydrogen evolution under sacrificial-donor conditions [YHW+25]. This precedent makes the proposed $3, 6, 9, 12$-connected chrysene network a mechanistically motivated candidate rather than an arbitrary chromophore. It does not, however, transfer the DBC rate, quantum yield, excited-state lifetime, or electronic structure to $\mathfrak{R}_N$.

The rectangular candidate differs from the benchmark in its molecular node, attachment-site coefficients, bridge lengths, lattice metric, pore geometry, and possible stacking arrangement. These differences enter explicitly through

$$a_N, \quad b_{N+2}, \quad T_x(E), \quad T_y(E), \quad \Delta G_{\text{CS}}, \quad \Delta G_{\text{H}},$$

and the associated kinetic parameters. The comparison is therefore based on a common mechanistic sequence and matched reaction boundary, not on presumed equality of material properties.

The unequal N- and $N+2$-segment bridges create anisotropy but do not prevent two-dimensional electronic communication. Within the reduced model,

$$T_x(E_*)T_y(E_*) \neq 0$$

implies nonzero band dispersion in both in-plane directions. The longer bridge may reduce T_y, but feasibility depends on whether the weaker coupling remains above the independently defined bottleneck threshold

$$t_{\min} \geq t_{\text{crit}},$$

rather than on whether the candidate bandwidth equals or exceeds the DBC bandwidth.

Geometric density and electronic dispersion are necessary structural advantages only when accompanied by optical excitation, favorable charge-separation energetics, carrier survival, catalyst access, and hydrogen-reduction alignment. The analysis therefore does not identify node density or visible absorption with photocatalytic activity.

11.2 Scope and limitations

The principal mathematical result is the certified lower bound

$$R_{\mathrm{H}_2,\mathfrak{R}} \geq R_{\mathfrak{R}}^{\mathrm{LB}},$$

under the hypotheses of Theorem 16. The experimentally relevant criterion is

$$R_{\mathfrak{R}}^{\mathrm{LB}} > R_{\mathrm{LOQ}},$$

not

$$R_{\mathfrak{R}}^{\mathrm{LB}} \geq R_{\mathrm{H}_2,\mathfrak{K}}.$$

Consequently, the model permits detectable candidate activity far below the DBC rate.

Several limitations bound this conclusion. First, $\mathfrak{R}_N$ is represented as an infinite, defect-free periodic lattice with one effective frontier state per node. Finite domain size, vacancies, linker defects, energetic disorder, grain boundaries, and nonperiodic stacking may reduce the calculated coupling and transport lengths. Second, the Bloch Hamiltonian retains only frozen nearest-neighbor couplings evaluated at E_*. Longer-range hopping, energy-dependent self-energies, interlayer coupling, excitonic effects, vibronic relaxation, and electron–phonon scattering are not resolved explicitly.

Third, the Marcus, diffusion–recombination, and sequential-branching models are reduced kinetic descriptions. Their use requires candidate-specific parameterization and validation. Correlated multielectron processes, heterogeneous platinum deposition, mass transport, proton activity near the catalyst, and evolving surface chemistry may violate the assumed factorization. The hydrogen-rate lower bound is valid only to the extent that its constituent lower and upper bounds are experimentally or computationally justified.

Fourth, the DBC material and $\mathfrak{R}_N$ may differ in surface area, wettability, porosity, optical scattering, platinum accessibility, and sample morphology even under the same formal reaction boundary. Matched ascorbate concentration, platinum loading, illumination, and temperature do not eliminate these material-dependent differences.

Finally, metal conditioning is optional and is not assumed to improve performance. Mg may alter electrostatic alignment or stacking without serving as a hydrogen-evolution catalyst. Fe, Co, or Ni may provide redox-active states but may also accelerate nonradiative relaxation. A metal-conditioned candidate must therefore satisfy the same free-energy, lifetime, transport, and detectability requirements as the unconditioned network.

11.3 Conclusion

This work has converted the proposed rectangular chrysene network into a falsifiable sequence of structural, electronic, thermodynamic, and kinetic tests. For fixed

$$N \in 2\mathbb{Z}_{\geq 0},$$

the $N/(N+2)$ construction has finite node density and admits direction-dependent effective couplings. If

$$T_x(E_*)T_y(E_*) \neq 0,$$

the reduced periodic Hamiltonian possesses two-dimensional dispersion. If, in addition,

$$\Delta G_{\mathrm{CS}} \leq -\delta_{\mathrm{CS}}, \qquad \chi_{\mathrm{Pt}} \leq 1, \qquad \Delta G_{\mathrm{H}} \leq -\delta_{\mathrm{H}},$$

and the measured kinetic bounds yield

$$R_{\mathfrak{R}}^{\mathrm{LB}} > R_{\mathrm{LOQ}},$$

then the model predicts a detectable Pt-assisted hydrogen-evolution signal under the declared sacrificial-donor conditions.

This conclusion is conditional but experimentally decisive: every required quantity can be computed, measured, or rejected prospectively. A positive controlled result would establish feasibility of the hydrogen-evolution half-reaction in the proposed material class. It would not establish catalyst-free hydrogen production, oxygen evolution, or overall water splitting. Those functions remain subsequent stages in the development of an integrated artificial-photosynthetic system.

A Literature Context and Relation to the Present Model

A.1 Conjugated organic frameworks for photocatalytic hydrogen evolution

Covalent organic frameworks provide a means of organizing molecular chromophores into periodic porous solids while controlling the identities of the nodes, linkers, pores, and stacking interfaces. Early experimental work established that such frameworks can support visible-light hydrogen evolution under sacrificial conditions. A hydrazone-linked COF produced hydrogen in the presence of a platinum cocatalyst and sacrificial electron donor [SSL14]. Subsequent azine-linked frameworks demonstrated that relatively small changes in molecular composition can alter optical absorption, electronic structure, and hydrogen-evolution activity [VHS+15]. Sulfone-containing COFs further showed that the chemical identity of the conjugated framework influences wettability, charge-carrier behavior, and photocatalytic performance [WCC+18].

These experiments establish an existence result for the material class: a crystalline organic framework can absorb visible light and deliver photogenerated electrons to a terminal hydrogen-evolution cocatalyst. They do not imply that every absorbing framework will evolve hydrogen. Absorption must be accompanied by energetically admissible charge separation, sufficiently slow recombination, electronic transport to an accessible interface, and electron transfer to the cocatalyst.

Fully conjugated carbon–carbon linkages are relevant because they can remove electronically insulating or hydrolytically vulnerable bonds from the in-plane transport pathway. Two-dimensional sp^2-carbon-conjugated frameworks have been synthesized with extended conjugation in two independent lattice directions and with optical properties determined jointly by the node, linker, and topology [JLG+18]. This precedent motivates the use of a common cyano-vinylene bridge in the present comparison. It does not, however, justify assuming that the two directional couplings are equal. In the rectangular chrysene lattice, the N-segment and $N+2$-segment bridges generally produce distinct effective couplings t_x and t_y.

A.2 Dibenzochrysene as the experimental benchmark

Dibenzo[g,p]chrysene has previously been incorporated into dual-pore COFs. The resulting frameworks exhibited controlled docking between layers and stabilization of photoexcited states, demonstrating that the extended aromatic node can participate in organized solid-state photophysics rather than acting only as an isolated molecular absorber [KSB+19].

More directly, Yu *et al.* reported a dibenzo[g,p]chrysene-based sp^2-carbon-linked COF with kagome topology and photocatalytic hydrogen evolution under visible-light, platinum-cocatalyzed, sacrificial-donor conditions [YHW+25]. The reported material combines a conjugated aromatic node, cyano-vinylene-type connectivity, periodic porosity, and stacked two-dimensional layers. It is therefore the closest presently identified experimental benchmark for the candidate considered here.

The benchmark supports the following limited inference:

$$\begin{gathered}\text{dibenzochrysene node} + \text{conjugated bridge} + \text{periodic lattice}\\ + \text{Pt} + \text{sacrificial donor} + \text{visible light} \implies R_{H_2} > 0\end{gathered}$$

for the particular synthesized and characterized DBC material. The present paper does not transfer the measured rate to the rectangular 3, 6, 9, 12-substituted chrysene network. Instead, it asks whether the candidate can satisfy a corresponding set of necessary electronic and kinetic conditions.

The structural change is substantial. The benchmark possesses kagome connectivity and a dibenzochrysene node, whereas the candidate possesses a rectangular graph, a smaller tetrasubstituted chrysene node, and unequal bridge lengths. Accordingly, topology, attachment-site frontier-orbital amplitudes, band dispersion, density, exciton behavior, and interfacial accessibility cannot be assumed invariant. These quantities enter the present model as explicit parameters or inequalities.

A.3 Charge separation and quantum efficiency

High hydrogen-evolution activity requires more than broad optical absorption. Donor–acceptor COFs have demonstrated that reducing exciton binding and improving the yield and lifetime of mobile charge carriers can produce high apparent quantum efficiencies under sacrificial photocatalytic conditions [LLL+22]. This observation supports separating the present feasibility analysis into the factors

$$\mathcal{A}, \qquad \Phi_{\mathrm{CS}}, \qquad \Phi_{\mathrm{tr}}, \qquad \Phi_{\mathrm{inj}}, \qquad \eta_{\mathrm{Pt}},$$

rather than identifying optical absorption with hydrogen production.

The thermodynamic charge-separation inequalities used in the main text are consistent with the Rehm–Weller treatment of photoinduced electron transfer [RW70]. The competition between charge transfer and recombination is represented using the nonadiabatic electron-transfer framework developed by Marcus [Mar93]. In its simplified form,

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|V|^2 \frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_{\mathrm{B}}T}\right],$$

the rate is nonzero whenever the electronic coupling V is nonzero and the remaining parameters are finite. The expression is used here as a conditional engineering relation, not as a quantitative prediction for a heterogeneous periodic solid. Disorder, exciton diffusion, solvent reorganization, surface states, and non-Markovian dynamics can require more complete treatments.

A.4 Cocatalyst placement and electron delivery

The platinum cocatalyst is not a passive normalization constant. Its loading, dispersion, binding environment, and position relative to electron-rich regions of a framework can change the probability of productive electron transfer. Spatially controlled photodeposition of platinum clusters on a COF has been shown to facilitate electron delivery and strongly influence measured hydrogen-evolution performance [LYH+22]. Consequently, the present lower-bound functional retains a separate interfacial factor η_{Pt}, and comparisons are meaningful only under matched or explicitly measured cocatalyst conditions.

This distinction also explains the use of the term *sacrificial hydrogen evolution*. The modeled experiment consumes a sacrificial electron donor to remove photogenerated holes and uses platinum to perform the terminal proton-reduction chemistry. It is therefore not an experiment in overall water splitting. General analyses of particulate photocatalysis likewise distinguish light absorption, charge generation, carrier transport, surface reaction, and the coupled oxidation and reduction half-reactions [WD20].

A.5 Metal-conditioned frameworks

Metal incorporation can alter frontier-state energies, excited-state lifetimes, charge localization, and transport without necessarily making the metal center the terminal hydrogen-evolution catalyst. In an isostructural series of porphyrin COFs containing Co, Ni, and Zn, metal identity changed charge-carrier dynamics and photocatalytic hydrogen-evolution activity while the frameworks retained similar topology [CWM+21]. This provides experimental precedent for treating metal identity as an electronic conditioning variable.

It does not establish that a metal confined within stacked chrysene layers will have the same function. A metal-conditioned chrysene model must specify, at minimum,

$$M, q_M, S_M, d_{M-\pi}, \text{coordination environment, counterions,}$$

where M, q_M, and S_M denote metal identity, oxidation state, and spin state. The resulting metal self-energy can shift or broaden the framework states and can either improve or impair the inequalities required for charge separation and electron delivery. The metal extension is therefore properly treated as a conditional perturbation of the metal-free model rather than as an assumed catalytic enhancement.

A.6 Unresolved question addressed by the present work

The literature establishes three relevant propositions:

1. conjugated organic frameworks can support sacrificial photocatalytic hydrogen evolution [SSL14, VHS+15, WCC+18];
2. dibenzochrysene-based frameworks can stabilize photoexcited states and, in a kagome sp^2-linked implementation, support measurable Pt-assisted hydrogen evolution [KSB+19, YHW+25]; and
3. charge separation, directional transport, cocatalyst coupling, and metal conditioning are independently consequential design variables [LLL+22, LYH+22, CWM+21].

The missing implication is

$$\text{DBC kagome activity} \quad \nRightarrow \quad \text{rectangular chrysene activity}$$

without additional assumptions. The purpose of the present analysis is to state those assumptions explicitly and derive falsifiable conditions under which

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} > 0$$

and, more stringently,

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}}.$$

Thus, the literature supplies experimental plausibility and parameter ranges; the mathematical model supplies the conditional bridge from the DBC benchmark to a prospective $3, 6, 9, 12$-connected rectangular chrysene network.

B Relation to the Chrysene-Origin Hypothesis

B.1 The strong chrysene-origin hypothesis

The present analysis may be placed within a broader hypothesis according to which substituted chrysene supplied a common molecular architecture for the origin and subsequent energetic development of living systems. This hypothesis has been developed through geometric, tensorial, operator-algebraic, and topological formulations of the substituted-chrysene network [Sch26f, Sch26e, Sch26a, Sch26c]. Its strongest form proposes not merely that chrysene-like aromatic compounds participated in prebiotic chemistry, but that a substituted-chrysene lattice served as a unified originator and persistent driver of biological organization [Sch26g].

Definition 30 (Strong chrysene-origin hypothesis)**.** *Let* H_{Ch} *denote the proposition that a chemically realizable class of substituted-chrysene assemblies supplied a common prebiotic architecture capable of supporting:*

(i) spatial organization and compartment-scale geometry;

(ii) encodable discrete molecular states;

(iii) environmental-energy absorption and transduction;

(iv) charge or excitation transport through an extended network;

(v) coupling of transported energy to chemical transformations;

(vi) persistence, copying, selection, or state-dependent reconstruction; and

(vii) an evolutionary continuation from prebiotic organization to increasingly complex biological matter.

The adjective strong *indicates the additional claim that these functions originated from one chrysene-centered material system rather than from several chemically independent originators.*

The hypothesis does not require every function to be performed by an unsubstituted chrysene molecule. It concerns a class of substituted, connected, stacked, metal-conditioned, and environmentally coupled chrysene assemblies. Substituents, bridges, ions, water, counterions, and surrounding molecules are therefore components of the admissible system rather than competing originators.

B.2 Mathematical representation of the network

The chrysene formalism was introduced to make the proposed molecular system amenable to mathematical analysis rather than leaving it solely as a structural analogy. A particular realization may be represented by the tuple

$$\mathfrak{C} = (G, \Lambda, \mathcal{H}, \mathcal{A}, H, \rho, \mathcal{L}, \mathcal{B}),$$

where:

1. $G = (V, E)$ is the molecular connection graph;
2. Λ is its geometric realization in $\mathbb{R}^2$ or $\mathbb{R}^3$;
3. $\mathcal{H}$ is an effective electronic or excitonic state space;
4. $\mathcal{A} \subseteq \mathcal{B}(\mathcal{H})$ is an algebra of observables or admissible transformations;
5. H is the electronic Hamiltonian;
6. ρ is a state or density operator;
7. $\mathcal{L}$ describes dissipative, environmental, or state-transition dynamics; and
8. $\mathcal{B}$ specifies chemical and energetic boundary conditions.

The graph G and its realization Λ encode attachment positions, bridge lengths, pores, stacking relations, and higher-order packing. The state space $\mathcal{H}$, observable algebra $\mathcal{A}$, and Hamiltonian H encode the corresponding electronic and quantum structure. This separation permits the topology, geometry, and electronic response to be varied independently and then related by explicit maps.

The operator-algebraic and cohomological components of this construction are developed in [Sch26a, Sch26c]. The tensorial and maximal-entropy formulation is described in [Sch26e], while geometric constraints on axis alignment, pore tethering, and side-chain packing are considered in [Sch26f, Sch26b]. Proposed topological, photonic, and quantum-information characteristics of the tetrasubstituted lattice are discussed in [Sch26d, Sch26g].

Within this representation, different physical questions correspond to different mathematical objects. For example,

$$\begin{aligned}
\text{topological structure} &\longleftrightarrow G,\ H_\bullet(G),\ H^\bullet(G),\\
\text{geometric packing} &\longleftrightarrow \Lambda,\ d_{ij},\ \theta_{ij},\\
\text{photonic response} &\longleftrightarrow H,\ \boldsymbol{\mu},\ \sigma_{\text{abs}}(\omega),\\
\text{electronic transport} &\longleftrightarrow (EI-H)^{-1},\ T_{ij}(E),\\
\text{quantum state structure} &\longleftrightarrow \mathcal{H},\ \mathcal{A},\ \rho,\\
\text{environmental dynamics} &\longleftrightarrow \mathcal{L},\ \mathcal{B}.
\end{aligned}$$

Here $H_\bullet(G)$ and $H^\bullet(G)$ denote graph-associated homological and cohomological structures, $\boldsymbol{\mu}$ is an effective transition-dipole operator, and $\sigma_{\text{abs}}(\omega)$ is an optical absorption response. The resolvent $(EI-H)^{-1}$ determines the bridge-mediated electronic couplings used in the present paper.

B.3 Photoactivity as a necessary plausibility condition

A system proposed as a persistent driver of prebiotic and biological organization must possess access to a nonequilibrium source of free energy. On the early Earth, incident solar radiation constitutes an abundant and spatially distributed source. A chrysene-origin hypothesis is therefore substantially more plausible if substituted-chrysene assemblies can do more than absorb light: they must retain, separate, transport, or chemically use some fraction of the absorbed excitation.

> **Definition 31** (Photochemical competence)**.** *Let P_{Ch} denote the proposition that at least one chemically realizable substituted-chrysene network and one physically admissible environment satisfy*
>
> $$\mathcal{A} > 0, \qquad \Phi_{\text{CS}} > 0, \qquad \Phi_{\text{tr}} > 0, \qquad \Phi_{\text{inj}} > 0,$$
>
> *where the quantities respectively represent photon absorption, charge separation, charge transport, and interfacial electron transfer.*
> *The network is called* photochemically competent *if these inequalities lead to a nonzero rate of a specified chemical output under explicitly stated boundary conditions.*

Photochemical competence is stronger than optical activity. A molecule may possess

$$\sigma_{\text{abs}}(\omega) > 0$$

while undergoing rapid radiative or nonradiative recombination, so that

$$\Phi_{\text{CS}}\Phi_{\text{tr}}\Phi_{\text{inj}} = 0.$$

Such a molecule would absorb light without supporting sustained chemical work. Consequently, absorption spectra alone cannot establish the energetic component of the chrysene-origin hypothesis.

Proposition 19 (Necessary-condition relation)**.** *Suppose that the strong chrysene-origin hypothesis requires solar energy to drive at least one of the chemical processes appearing in Definition 30. Then*

$$\mathsf{H}_{\mathrm{Ch}} \Longrightarrow \mathsf{P}_{\mathrm{Ch}}.$$

Equivalently,

$$\neg\mathsf{P}_{\mathrm{Ch}} \Longrightarrow \neg\mathsf{H}_{\mathrm{Ch}}$$

for every version of the hypothesis in which chrysene is the solar-energy transducer.

Proof. Assume H_{Ch}. By hypothesis, the chrysene system is a driver of chemical organization and solar radiation is one of its required nonequilibrium energy sources. If P_{Ch} were false, then every chemically realizable chrysene network would have zero yield for at least one indispensable stage among absorption, charge separation, transport, and interfacial transfer. The net solar-to-chemical conversion yield would consequently vanish. The system could not perform the assumed solar-driven chemical work, contradicting H_{Ch}. Therefore, $\mathsf{H}_{\mathrm{Ch}} \Rightarrow \mathsf{P}_{\mathrm{Ch}}$. The second implication is its contrapositive. □

The converse does not hold:

$$\mathsf{P}_{\mathrm{Ch}} \quad \not\Rightarrow \quad \mathsf{H}_{\mathrm{Ch}}.$$

Demonstrating photoinduced charge transport or hydrogen evolution would establish only one necessary capability. It would not establish prebiotic availability, self-assembly, information encoding, replication, evolutionary continuity, or the exclusivity implied by the word *sole*.

B.4 Role of the present hydrogen-evolution analysis

The present paper addresses a restricted instance of P_{Ch}. It considers whether a $3, 6, 9, 12$-connected rectangular chrysene network can satisfy the electronic and kinetic inequalities required to deliver photogenerated electrons to a platinum hydrogen-evolution sink under sacrificial-donor conditions. Its principal conditional statement has the form

$$Q_{\mathrm{opt}} \wedge Q_{\mathrm{CS}} \wedge Q_{\mathrm{tr}} \wedge Q_{\mathrm{inj}} \wedge Q_{\mathrm{Pt}} \Longrightarrow R^{\mathrm{LB}}_{\mathfrak{R}_N} > 0.$$

This is not a claim that the proposed lattice has already been shown to produce hydrogen. Rather, it identifies a finite collection of measurable conditions under which a nonzero output follows within the model. Comparison with the experimentally studied dibenzochrysene framework supplies a relevant external benchmark because dibenzochrysene COFs have exhibited stabilized photoexcited states and Pt-assisted photocatalytic hydrogen evolution [KSB+19, YHW+25].

Hydrogen evolution is used as an experimentally legible reporter of electron delivery. In the present boundary-value problem,

$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H}_2$$

demonstrates that photogenerated reducing equivalents have survived long enough to reach an interface and participate in chemical bond formation. Accordingly, a positive controlled experiment would support the proposition that the chrysene architecture can couple optical excitation to chemical output.

It would not establish catalyst-free hydrogen production, overall water splitting, or an autonomous prebiotic photosystem. Platinum and the sacrificial donor externalize important catalytic and oxidative functions. Their use is nevertheless appropriate at the present stage because it isolates the narrower question of whether the chrysene network can absorb light, separate charge, and deliver electrons.

B.5 Connection with the encoded lattice program

The broader chrysene formalism proposes that substitution positions and network connections can define a molecularly encodable state space [Sch26d, Sch26g]. In this interpretation, the attachment sites

$$\{3, 6, 9, 12\}$$

are not merely synthetic handles. They specify directional relations through which local molecular states may be extended into a periodic graph. Bridge identity, bridge length, substituent identity, metal occupancy, stacking distance, and environmental state then form a parameter vector

$$\Theta = \left(N_x, N_y, \mathbf{s}, M, q_M, S_M, d_{\pi\pi}, \boldsymbol{\varepsilon}_{\mathrm{env}}\right).$$

The resulting map

$$\Theta \longmapsto \left(\sigma_{\mathrm{abs}}, E_{\mathrm{ex}}, \Delta G_{\mathrm{CS}}, t_x, t_y, k_{\mathrm{tr}}, k_{\mathrm{rec}}, R_{\mathrm{chem}}\right)$$

connects the formal network description to experimentally measurable photochemical properties. This is the precise point at which the abstract chrysene formalism encounters physical falsifiability.

The related patent describes encoded design and integrated synthesis involving nucleic acids, phospholipids, and associated molecular products [Sch25]. The patent establishes a claimed technological and synthetic domain; it should not be treated as independent experimental evidence for the origin-of-life hypothesis. Its relevance here is that it illustrates how positional encoding and molecular construction may be translated into realizable chemical designs.

B.6 Evidentiary status and research sequence

The cited chrysene-formalism publications primarily define the hypothesis and its mathematical architecture. Because they arise from the same theoretical program, they provide internal coherence rather than independent empirical confirmation. The DBC literature supplies a related but chemically distinct experimental precedent. Neither category alone establishes the strong chrysene-origin hypothesis.

A disciplined research sequence is therefore

$$\begin{aligned}\text{formal network} &\longrightarrow \text{electronic feasibility}\\ &\longrightarrow \text{prospective photoactivity}\\ &\longrightarrow \text{chemical energy conversion}\\ &\longrightarrow \text{autonomous coupled chemistry}\\ &\longrightarrow \text{prebiotic replication and selection.}\end{aligned}$$

The present work occupies the second step and defines tests for the third. A prospective demonstration of controlled, light-dependent hydrogen evolution would not prove the entire sequence, but it would remove a central plausibility objection: that substituted-chrysene networks are merely light-absorbing structures without a route to separated charge or chemical work.

Conversely, failure to satisfy the optical, redox, transport, or recombination inequalities over the chemically accessible design space would substantially narrow, and could falsify, the solar-energy-transduction branch of the hypothesis. The present analysis is therefore consistent with the larger chrysene-origin literature precisely because it converts one of its indispensable physical assumptions into a bounded and experimentally contestable proposition.

References

[CWM+21] Rufan Chen, Yang Wang, Yuan Ma, Arindam Mal, Xiao-Ya Gao, Lei Gao, Lijie Qiao, Xu-Bing Li, Li-Zhu Wu, and Cheng Wang. Rational design of isostructural 2D porphyrin-based covalent organic frameworks for tunable photocatalytic hydrogen evolution. *Nature Communications*, 12:1354, 2021.

[JLG+18] Enquan Jin, Juan Li, Keyu Geng, Qiuhong Jiang, Hong Xu, Qing Xu, and Donglin Jiang. Designed synthesis of stable light-emitting two-dimensional sp2 carbon-conjugated covalent organic frameworks. *Nature Communications*, 9:4143, 2018.

[KSB+19] Niklas Keller, Torben Sick, Nicolai N. Bach, Andreas Koszalkowski, Julian M. Rotter, Dana D. Medina, and Thomas Bein. Dibenzochrysene enables tightly controlled docking and stabilizes photoexcited states in dual-pore covalent organic frameworks. *Nanoscale*, 11(48):23338–23345, 2019.

[LLL+22] Chunzhi Li, Jiali Liu, He Li, Kaifeng Wu, Junhui Wang, and Qihua Yang. Covalent organic frameworks with high quantum efficiency in sacrificial photocatalytic hydrogen evolution. *Nature Communications*, 13:2357, 2022.

[LYH+22] Yimeng Li, Li Yang, Huijie He, Lei Sun, Honglei Wang, Xu Fang, Yanliang Zhao, Daoyuan Zheng, Yu Qi, Zhen Li, and Weiqiao Deng. In situ photodeposition of platinum clusters on a covalent organic framework for photocatalytic hydrogen production. *Nature Communications*, 13:1355, 2022.

[Mar93] Rudolph A. Marcus. Electron transfer reactions in chemistry: Theory and experiment. *Reviews of Modern Physics*, 65(3):599–610, 1993.

[RW70] Dieter Rehm and Albert Weller. Kinetics of fluorescence quenching by electron and H-atom transfer. *Israel Journal of Chemistry*, 8(2):259–271, 1970.

[Sch25] Charles D. Schaper. Encoded design integrated synthesis of nucleic acids, and phospholipids, and related pharmaceutical products, 2025. Patent US 12,195,423.

[Sch26a] Charles D. Schaper. *Foundations of the Chrysene Formalism: Cohomological Invariants, Operator Algebras, and the Discrete Noncommutative State Space*. Schaper Systems Press, San Francisco, CA, 2026. ISBN: 979-8-950371-08-0.

[Sch26b] Charles D. Schaper. Higher-order geometry of the abiotic loom: Axis alignment, pore tethering, and side-chain packing of secondary-structure elements in the chrysene tensor space. *Annals of the Chrysene Formalism*, 1:277–288, 2026.

[Sch26c] Charles D. Schaper. On the foundations of discrete non-commutative topoi: Operator algebras, $\mathbb{F}_4$ sequence spaces, and the c_{2h} bipartite isomorphism. *Annals of the Chrysene Formalism*, 1:130–142, 2026.

[Sch26d] Charles D. Schaper. Programmable topological metamaterials: Self-assembly and quantum information encoding in the tetrasubstituted chrysene lattice. *Annals of the Chrysene Formalism*, 1:169–177, 2026.

[Sch26e] Charles D. Schaper. *Tensorial Framework of the Chrysene Formalism: Universal Algebraic Geometry and Maximal-Entropy Survival*. Schaper Systems Press, San Francisco, CA, 2026. ISBN: 979-8-950371-03-5.

[Sch26f] Charles D. Schaper. *The Geometric Origins of Life: The Chrysene Formalism and the Algebraic Foundations of the Biosphere*. Schaper Systems Press, San Francisco, CA, 2026. ISBN: 979-8-950371-02-8.

[Sch26g] Charles D. Schaper. The universal blueprint: One encodable topological metamaterial to explain the origin, intelligence, and evolution of life. *Annals of the Chrysene Formalism*, 1:178–195, 2026.

[SSL14] Linus Stegbauer, Katharina Schwinghammer, and Bettina V. Lotsch. A hydrazone-based covalent organic framework for photocatalytic hydrogen production. *Chemical Science*, 5(7):2789–2793, 2014.

[VHS+15] Vijay S. Vyas, Frederik Haase, Linus Stegbauer, Gökcen Savasci, Filip Podjaski, Christian Ochsenfeld, and Bettina V. Lotsch. A tunable azine covalent organic framework platform for visible light-induced hydrogen generation. *Nature Communications*, 6:8508, 2015.

[WCC+18] Xiaoyan Wang, Linjiang Chen, Samantha Y. Chong, Marc A. Little, Yongzhen Wu, Wei-Hong Zhu, Rob Clowes, Yong Yan, Martijn A. Zwijnenburg, Reiner Sebastian Sprick, and Andrew I. Cooper. Sulfone-containing covalent organic frameworks for photocatalytic hydrogen evolution from water. *Nature Chemistry*, 10(12):1180–1189, 2018.

[WD20] Qian Wang and Kazunari Domen. Particulate photocatalysts for light-driven water splitting: Mechanisms, challenges, and design strategies. *Chemical Reviews*, 120(2):919–985, 2020.

[YHW+25] Jun-Jie Yu, Xin Huang, Li-Ying Wang, Yan-Ze Wu, Zhi-Wei Huang, Ling-Ling Su, Nan-Nan Wang, Ji-Pan Yu, and Wei-Qun Shi. Topology-templated synthesis of dibenzo[g, p]chrysene-based sp2 carbon-linked covalent organic frameworks with kagome lattice for enhanced photocatalytic hydrogen evolution. *Advanced Materials*, 37(44):e04808, 2025.