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Computational Feasibility of a Rectangular Chrysene Network: Comparison with a Dibenzochrysene Kagome Benchmar

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

Abstract

This Supplemental Information provides the calculation and reproducibility framework supporting the conditional feasibility analysis of a 3, 6, 9, 12-connected rectangular chrysene network. A provenance system distinguishes analytically defined, prospectively fixed, computed, measured, and literature-sourced quantities. Tridiagonal determinant recurrences and transfer matrices describe bridge-mediated electronic coupling for N- and $N + 2$-segment directions. A homogeneous reduction gives closed-form Chebyshev expressions for propagating, band-edge, and off-resonant coupling regimes and defines the admissible set of bridge orders satisfying the minimum two-direction coupling threshold. Primitive-cell accounting separates geometric density from density per unit mass and establishes the effects of bridge length, metals, counterions, and retained species on mass-normalized optical and hydrogen-evolution rates. Deterministic intervals, simultaneous confidence bounds, covariance-aware logarithmic propagation, and joint resampling procedures are developed for the hydrogen-rate lower bound. Metal ions are represented through an energy-dependent Schur-complement self-energy that permits calculation of energetic shifts, directional-coupling perturbations, induced broadening, and the competition between productive charge separation and excited-state quenching. A prospective calculation sequence specifies candidate locking, numerical verification, uncertainty calibration, controlled measurement, and archival requirements. These results define reproducible conditions for selecting and testing candidate networks; they do not establish candidate-specific hydrogen production, catalyst-free proton reduction, water oxidation, or overall water splitting.

Keywords: substituted chrysene; rectangular molecular network; supplemental information; bridge Hamiltonian; transfer matrix; Green's-function reduction; Chebyshev recurrence; anisotropic electronic coupling; mass-normalized density; uncertainty propagation; metal-ion conditioning; photocatalytic hydrogen evolution; artificial photosynthesis; computational reproducibility.

1 Introduction

The associated article formulates a conditional feasibility test for a periodic network constructed from 3, 6, 9, 12-functionalized chrysene nodes. For fixed

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

the candidate contains an N-order bridge in the C3–C9 direction and an $N+2$-order bridge in the C12–C6 direction. The resulting lattice is rectangular rather than metrically square and may possess unequal geometric, electronic, and transport properties in its two in-plane directions.

The principal question is not whether the candidate must equal or exceed the published dibenzochrysene kagome benchmark. It is whether at least one chemically realizable candidate can satisfy a prospectively declared set of conditions sufficient to predict and subsequently detect Pt-assisted hydrogen evolution under sacrificial-donor conditions. In abbreviated form, these conditions include

$$\min\left\{|T_x(E^*)|,\ |T_y(E^*)|\right\} \geq t_{\mathrm{crit}},$$
$$\Delta G_{\mathrm{CS}} \leq -\delta_{\mathrm{CS}}, \qquad \Delta G_H \leq -\delta_H,$$
$$\underline{\Phi}_{\mathrm{CS}} \geq \phi_{\mathrm{CS,min}}, \qquad \chi_{\mathrm{Pt}} \leq 1, \qquad R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}}.$$

Each inequality must be supported by candidate-specific calculations, measurements, or calibrated uncertainty bounds. No geometric, electronic, or kinetic parameter is inherited solely from the common chrysene character of the candidate and benchmark.

The main article contains the logical definitions, propositions, and proofs establishing the conditional relationship between

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these quantities. The purpose of this Supplemental Information is narrower and computational: it specifies how the required parameters are to be constructed, normalized, propagated, verified, and archived. In particular, it addresses five questions that arise when the analytical conditions are applied to an actual candidate:

1. How does the addition of two effective conjugated segments alter the directional bridge-mediated coupling?

2. How should primitive-cell composition be converted into mass-normalized node, bridge, photon-absorption, and hydrogen-evolution quantities?

3. How can uncertainty in multiplicative optical, kinetic, transport, and interfacial factors be propagated into a simultaneous rate lower bound?

4. Under what perturbative conditions can a caged metal ion change electronic alignment or transport without introducing prohibitive excited-state quenching?

5. What information must be fixed and retained so that a prospective candidate decision can be reproduced independently?

Section 2 defines the notation, provenance classes, and calculation conventions. Section 3 develops the bridge determinant recurrence, transfer matrices, homogeneous Chebyshev reduction, and dependence on N. Section 4 distinguishes geometric density from density per unit mass and derives the primitive-cell normalization. Section 5 constructs deterministic and probabilistic lower bounds while retaining covariance and assay-threshold uncertainty. Section 6 treats metal conditioning through an energy-dependent self-energy and an explicit charge-separation–quenching competition. Section 7 provides the calculation, candidate-locking, verification, and archival sequence.

The extended square-lattice formalism is supplied separately as companion supporting theory. It is not required for the calculations presented here. Likewise, the full DBC kagome Hamiltonian and a general literature review are not reproduced. The DBC material supplies experimental precedent and matched reaction conditions, whereas all candidate conclusions are derived from the rectangular network and its own parameter record.

The scope remains restricted to the reductive half-reaction

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

with platinum as the terminal hydrogen-evolution cocatalyst and a sacrificial donor removing oxidizing equivalents. Nothing in this supplement establishes catalyst-free proton reduction, water oxidation, oxygen evolution, sacrificial-donor-free operation, or integrated overall water splitting.

2 Notation, Parameter Provenance, and Calculation Conventions

This supplement uses the notation of the main article. No candidate-specific geometric, electronic, kinetic, or catalytic parameter is transferred from the DBC benchmark to the rectangular chrysene candidate. Literature values define comparison conditions or prior ranges only; every quantity entering the candidate feasibility decision must be calculated, measured, or fixed prospectively.

Definition 1 (Rectangular candidate and bridge orders)**.** *Fix*

$$N \in 2\mathbb{Z}_{\geq 0}, \qquad m_x := N, \qquad m_y := N + 2.$$

The symbol $\mathfrak{R}_N$ denotes the periodic $3, 6, 9, 12$-connected chrysene network having attachment rules

$$\mathrm{C3}(i, j) \longleftrightarrow \mathrm{C9}(i{+}1, j), \qquad \mathrm{C12}(i, j) \longleftrightarrow \mathrm{C6}(i, j{+}1),$$

through bridges of orders m_x and m_y, respectively. Its primitive translation lengths are denoted by

$$a_N > 0, \qquad b_{N+2} > 0,$$

and its primitive-cell area is

$$A_N := a_N b_{N+2}.$$

The symbols a_N and b_{N+2} denote optimized center-to-center distances; they are not assumed to be proportional to the nominal segment counts.

Definition 2 (Bridge-mediated coupling)**.** *For $m \in \{N, N+2\}$, let*

$$H_B^{(m)} : \mathcal{H}_B^{(m)} \longrightarrow \mathcal{H}_B^{(m)}$$

be the effective bridge Hamiltonian. Whenever $E \notin \mathrm{Spec}(H_B^{(m)})$, define

$$T_x(E; N) := \mathbf{v}_3^\dagger \left(EI - H_B^{(N)}\right)^{-1} \mathbf{v}_9,$$
$$T_y(E; N) := \mathbf{v}_{12}^\dagger \left(EI - H_B^{(N+2)}\right)^{-1} \mathbf{v}_6.$$

At the predeclared comparison energy E^*, write

$$t_x := |T_x(E^*; N)|, \qquad t_y := |T_y(E^*; N)|, \qquad t_{\min} := \min\{t_x, t_y\}.$$

The directional anisotropy ratio is

$$\eta_T(N) := \frac{t_y}{t_x},$$

provided $t_x > 0$. No equality between t_x and t_y is assumed.

Definition 3 (Rate lower bound and decision quantity)**.** *Let*

$$\underline{\mathcal{A}}_N, \quad \underline{\Phi}_{\mathrm{CS},N}, \quad \underline{\Phi}_{\mathrm{tr},N}, \quad \underline{\Phi}_{\mathrm{inj},N}, \quad \underline{\eta}_{\mathrm{Pt},N}$$

denote simultaneous one-sided lower bounds for absorbed-photon input, charge separation, carrier transport, electron injection, and productive platinum utilization. The hydrogen-evolution lower bound is

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} := \frac{1}{2}\underline{\mathcal{A}}_N \underline{\Phi}_{\mathrm{CS},N} \underline{\Phi}_{\mathrm{tr},N} \underline{\Phi}_{\mathrm{inj},N} \underline{\eta}_{\mathrm{Pt},N}.$$

The factor $1/2$ *accounts for the two-electron stoichiometry of*

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

The prospective detectability margin is

$$\mathscr{M}_N := R^{\mathrm{LB}}_{\mathfrak{R}_N} - R_{\mathrm{LOQ}},$$

where $R_{\mathrm{LOQ}} > 0$ *is the independently determined, background-corrected assay limit of quantification. Detectable feasibility requires*

$$\mathscr{M}_N > 0.$$

Definition 4 (Provenance classes)**.** *Every parameter* q *is assigned a provenance record*

$$\Pi(q) = \big(\mathrm{class}(q), \mathrm{method}(q), \mathrm{conditions}(q), \mathrm{uncertainty}(q)\big),$$

where

$$\mathrm{class}(q) \in \{\mathsf{An}, \mathsf{Pr}, \mathsf{Co}, \mathsf{Me}, \mathsf{Li}\}.$$

The classes denote, respectively, an analytical definition or derived identity, a prospectively fixed design or threshold, a computed quantity, a measured quantity, and a literature-sourced quantity. A quantity may have more than one class when, for example, a computed prediction is subsequently tested experimentally.

Definition 5 (Calculation conventions)**.** *The following conventions apply throughout the supplement.*

1. *Energies are reported in electronvolts, wavelengths in nanometers, distances in Ångströms, potentials in volts, and mass-normalized hydrogen-evolution rates in* $\mathrm{mol\,g^{-1}\,h^{-1}}$*, unless stated otherwise.*
2. *Every electrochemical potential is accompanied by its reference electrode, pH, solvent, electrolyte, and conversion rule. Potentials referenced to different scales are not combined before conversion to a common scale.*
3. *An underlined quantity denotes a one-sided simultaneous lower bound; an overlined quantity denotes a corresponding upper bound. Point estimates are not substituted for bounds in a certified detectability calculation.*
4. *The comparison energy* E^**, uncertainty level* $1-\alpha$*, coupling threshold* t_{crit}*, energetic margins* δ_{CS} *and* δ_H*, and* R_{LOQ} *are fixed before the prospective hydrogen measurements are unblinded.*
5. *Proprietary calibration data and untouched validation data remain disjoint. No external-validation observation may be used to select a candidate, tune a model, or revise a decision threshold.*
6. *Literature values from the DBC benchmark define mechanistic precedent and matched boundary conditions only. In particular,*

$$q_{\mathfrak{K}} \neq q_{\mathfrak{R}_N}$$

unless equality is established independently for the stated quantity.

7. *All calculations concern Pt-assisted sacrificial hydrogen evolution. Catalyst-free proton reduction, water oxidation, and integrated overall water splitting remain excluded.*

Table 1: Primary provenance of quantities used in the supplemental calculations.

Quantity	Class	Required provenance record
N, m_x, m_y	Pr	Candidate definition fixed before prospective testing.
a_N, b_{N+2}	Co/Me	Optimized geometry; structural measurement if synthesized.
$H_B^{(m)}, \mathbf{v}_r, T_\alpha$	Co	Electronic-structure method, basis, geometry, and energy reference.
$\mathcal{A}_N, E_{00}$	Co/Me	TD-DFT prediction and calibrated optical spectroscopy.
$\Delta G_{\mathrm{CS}}, \Delta G_H$	Co/Me	Declared potential reference, environment, and uncertainty interval.
$\Phi_{\mathrm{CS}}, \Phi_{\mathrm{tr}}, \Phi_{\mathrm{inj}}$	Me/Co	Time-resolved, transport, and interfacial determinations or calibrated bounds.
η_{Pt}	Me/Pr	Pt loading, deposition state, accessible-site model, and controls.
R_{LOQ}	Me/Pr	Blank distribution, calibration procedure, confidence level, and replicate plan.
DBC quantities	Li	Published benchmark values and reaction conditions; not candidate parameters.
Metal variables	Pr/Co/Me	Identity, oxidation and spin state, geometry, counterions, and environment.

Remark 1 (Logical role of the supplement)**.** *The calculations below evaluate the consequences of declared structural and physical assumptions. They do not replace candidate synthesis or prospective measurement. Their purpose is to identify the parameter regions for which*

$$t_{\min} \geq t_{\mathrm{crit}} \qquad \text{and} \qquad R^{\mathrm{LB}}_{\mathfrak{R}_N} > R_{\mathrm{LOQ}}$$

can be supported without transferring the experimental performance of the DBC benchmark to $\mathfrak{R}_N$.

3 Bridge Recurrence, Transfer Matrices, and Dependence on N

The purpose of this section is to make explicit how the two additional effective conjugated segments in the y-direction alter the bridge-mediated coupling. The treatment is first stated for a nonuniform nearest-neighbor bridge and then reduced to a homogeneous model admitting closed-form expressions. These expressions are reduced models; candidate certification requires replacement of their parameters by candidate-specific electronic-structure calculations.

3.1 General tridiagonal bridge recurrence

Definition 6 (Reduced bridge Hamiltonian)**.** *Let* $\ell_0 \geq 1$ *denote the number of effective frontier states assigned to the reference crossbar. A bridge of extension order* $m \in 2\mathbb{Z}_{\geq 0}$ *is represented by*

$$L_m := \ell_0 + m$$

effective states. Thus, $m = 0$ *denotes the reference crossbar and does not denote the absence of a chemical connection. On the orthonormal basis*

$$\{|1\rangle, \ldots, |L_m\rangle\},$$

define

$$H_B^{(m)} = \sum_{j=1}^{L_m} \varepsilon_j \, |j\rangle\langle j| + \sum_{j=1}^{L_m-1} \left(\tau_j \, |j\rangle\langle j+1| + \overline{\tau_j} \, |j+1\rangle\langle j|\right),$$

where $\varepsilon_j \in \mathbb{R}$ *and* $\tau_j \in \mathbb{C} \setminus \{0\}$.

For $1 \leq r \leq L_m$, let $H_{B,r}$ denote the leading $r \times r$ principal submatrix of $H_B^{(m)}$, and define

$$D_r(E) := \det\left(EI_r - H_{B,r}\right).$$

Lemma 1 (Continuant recurrence)**.** *The bridge determinants satisfy*

$$D_0(E) = 1, \qquad D_1(E) = E - \varepsilon_1,$$

and, for $r \geq 2$,

$$D_r(E) = (E - \varepsilon_r)\, D_{r-1}(E) - |\tau_{r-1}|^2 D_{r-2}(E).$$

Proof. Expansion of $\det\left(EI_r - H_{B,r}\right)$ along its final row leaves the leading $(r-1)\times(r-1)$ determinant and the product of the two entries coupling sites $r-1$ and r. The first contribution is $(E-\varepsilon_r)D_{r-1}(E)$; the second is $-|\tau_{r-1}|^2 D_{r-2}(E)$. □

Proposition 2 (Endpoint Green's function)**.** *Suppose*

$$E \notin \mathrm{Spec}\left(H_B^{(m)}\right).$$

Then

$$\langle 1| \left(EI - H_B^{(m)}\right)^{-1} |L_m\rangle = \frac{\prod_{j=1}^{L_m-1} \tau_j}{D_{L_m}(E)}.$$

Consequently, if $\gamma_{L,m}$ *and* $\gamma_{R,m}$ *are the node–bridge endpoint couplings, then*

$$T_m(E) = \overline{\gamma_{L,m}}\, \gamma_{R,m} \frac{\prod_{j=1}^{L_m-1} \tau_j}{D_{L_m}(E)}.$$

Proof. By Cramer's rule, the $(1, L_m)$ matrix element of the inverse is the corresponding cofactor divided by $D_{L_m}(E)$. Because the bridge is tridiagonal and contains a single nearest-neighbor path between its endpoints, the cofactor is $\prod_{j=1}^{L_m-1} \tau_j$. Multiplication by the left and right node–bridge matrix elements gives the asserted effective coupling. □

Remark 2 (Scope of the single-path reduction)**.** *The numerator in Proposition 2 cannot vanish when every* $\tau_j \neq 0$. *Therefore, a transmission zero arising from destructive interference is not represented by this single-path chain. Candidate-specific antiresonances caused by multiple orbitals, pendant groups, or parallel pathways must be determined from the full matrix*

$$\mathbf{v}_L^{\dagger} \left(EI - H_B^{(m)}\right)^{-1} \mathbf{v}_R.$$

Observation of such an antiresonance invalidates the homogeneous single-channel approximation at the corresponding energy.

3.2 Transfer-matrix representation

Let $\psi_j = \langle j|\psi|j|\psi\rangle$. The stationary bridge equation $H_B^{(m)}|\psi\rangle = E|\psi\rangle$ gives

$$\tau_j\psi_{j+1} = (E-\varepsilon_j)\psi_j - \overline{\tau_{j-1}}\psi_{j-1}.$$

Whenever $\tau_j \neq 0$, define

$$\mathsf{M}_j(E) := \begin{pmatrix} \dfrac{E-\varepsilon_j}{\tau_j} & -\dfrac{\overline{\tau_{j-1}}}{\tau_j} \\ 1 & 0 \end{pmatrix}.$$

Then

$$\begin{pmatrix}\psi_{j+1}\\ \psi_j\end{pmatrix} = \mathsf{M}_j(E)\begin{pmatrix}\psi_j\\ \psi_{j-1}\end{pmatrix}.$$

Definition 7 (Bridge transfer matrix)**.** *The transfer matrix of an m-order bridge is*

$$\mathsf{P}_m(E) := \mathsf{M}_{L_m}(E)\mathsf{M}_{L_m-1}(E)\cdots\mathsf{M}_1(E).$$

It maps the left boundary data to the right boundary data:

$$\begin{pmatrix}\psi_{L_m+1}\\ \psi_{L_m}\end{pmatrix} = \mathsf{P}_m(E)\begin{pmatrix}\psi_1\\ \psi_0\end{pmatrix}.$$

The ordered product $\mathsf{P}_m(E)$ is the appropriate quantity for a chemically nonuniform bridge. In particular, changes in linker identity, torsion, heteroatom substitution, or local electrostatic environment may be represented through site-dependent ε_j and τ_j.

3.3 Homogeneous bridge and closed-form solution

For analytical comparison, assume

$$\varepsilon_j = \varepsilon_B, \qquad \tau_j = t_B > 0$$

for every internal bridge site. A one-dimensional gauge transformation has been used to make the homogeneous hopping parameter real and positive. Set

$$z(E) := \frac{E-\varepsilon_B}{2t_B}.$$

Proposition 3 (Chebyshev representation)**.** *For a homogeneous bridge of L effective states,*

$$D_L(E) = t_B^L U_L(z(E)),$$

where U_L is the Chebyshev polynomial of the second kind.

Hence

$$G_{1L}(E) := \langle 1|(EI-H_B)^{-1}|L\rangle = \frac{1}{t_B U_L(z(E))}$$

and

$$T_L(E) = \frac{\overline{\gamma_L}\gamma_R}{t_B U_L(z(E))}.$$

Proof. The determinant recurrence becomes

$$D_L(E) = 2t_B z(E) D_{L-1}(E) - t_B^2 D_{L-2}(E).$$

After writing $D_L = t_B^L Q_L$, one obtains

$$Q_L = 2zQ_{L-1} - Q_{L-2}, \qquad Q_0 = 1, \qquad Q_1 = 2z.$$

These are the defining recurrence and initial conditions for $U_L(z)$. The Green's-function identity follows from Proposition 2. □

For the homogeneous transfer matrix,

$$\mathsf{M}(E) = \begin{pmatrix} 2z(E) & -1 \\ 1 & 0 \end{pmatrix}, \qquad \det\mathsf{M}(E) = 1,$$

and

$$\mathsf{P}_m(E) = \mathsf{M}(E)^{L_m}.$$

Its eigenvalues are

$$\lambda_\pm(E) = z(E) \pm \sqrt{z(E)^2-1}, \qquad \lambda_+(E)\lambda_-(E) = 1.$$

Corollary 1 (Propagating, edge, and evanescent regimes)**.** *For real E, the homogeneous bridge has the following three regimes.*

1. *If $|z(E)| < 1$, write $z(E) = \cos k$, with $k \in (0,\pi)$. Then*
$$U_L(z) = \frac{\sin((L+1)k)}{\sin k}$$
and
$$T_L(E) = \frac{\overline{\gamma_L}\gamma_R}{t_B}\frac{\sin k}{\sin((L+1)k)}.$$
2. *If $|z(E)| = 1$, then*
$$|U_L(z)| = L+1$$
and therefore
$$|T_L(E)| = \frac{|\gamma_L\gamma_R|}{t_B(L+1)}.$$
3. *If $|z(E)| > 1$, write $|z(E)| = \cosh\kappa$, with $\kappa > 0$. Then*
$$|U_L(z)| = \frac{\sinh((L+1)\kappa)}{\sinh\kappa}$$

and

$$|T_L(E)| = \frac{|\gamma_L \gamma_R|}{t_B} \frac{\sinh \kappa}{\sinh((L+1)\kappa)}.$$

The third case gives the asymptotic relation

$$|T_L(E)| = O\left(e^{-L\kappa}\right), \qquad L \longrightarrow \infty.$$

Thus, two additional off-resonant segments impose an asymptotically finite multiplicative penalty rather than forcing the coupling identically to zero.

Remark 3 (Regularization near bridge resonances)**.** *If*

$$U_L(z(E)) = 0,$$

then E is an eigenvalue of the isolated bridge and the reduced resolvent has a pole. The divergence does not represent an infinite physical node-to-node coupling. Contact self-energies, environmental broadening, and hybridization must be retained. A minimal regularization replaces

$$E \longmapsto E + \frac{i\Gamma_B}{2}, \qquad \Gamma_B > 0,$$

before evaluating the Green's function. Candidate decisions shall not be based on an unregularized isolated-bridge pole.

3.4 Directional dependence on N

For the rectangular network, set

$$L_x(N) := \ell_0 + N, \qquad L_y(N) := \ell_0 + N + 2.$$

Define the attachment-site factor

$$\chi_\gamma(E;N) := \frac{|\gamma_{12,L}(E;N)\gamma_{6,R}(E;N)|}{|\gamma_{3,L}(E;N)\gamma_{9,R}(E;N)|}.$$

This factor retains differences between the C3–C9 and C12–C6 frontier-orbital amplitudes even when the internal crossbar parameters are identical.

Proposition 4 (Directional-coupling ratio)**.** *Under the homogeneous bridge approximation,*

$$\eta_T(E;N) := \frac{|T_y(E;N)|}{|T_x(E;N)|} = \chi_\gamma(E;N) \left| \frac{U_{\ell_0+N}(z(E))}{U_{\ell_0+N+2}(z(E))} \right|.$$

In particular, equality of the crossbar chemistry does not imply $\eta_T(E;N) = 1$.

Proof. Apply Proposition 3 separately to bridge lengths $L_x(N)$ and $L_y(N)$, and divide the magnitudes of the resulting couplings. The common factor t_B^{-1} cancels, while the endpoint couplings produce $\chi_\gamma(E;N)$. □

For the first four admissible values of N,

$$\eta_T(E;0) = \chi_\gamma(E;0) \left| \frac{U_{\ell_0}(z)}{U_{\ell_0+2}(z)} \right|,$$
$$\eta_T(E;2) = \chi_\gamma(E;2) \left| \frac{U_{\ell_0+2}(z)}{U_{\ell_0+4}(z)} \right|,$$
$$\eta_T(E;4) = \chi_\gamma(E;4) \left| \frac{U_{\ell_0+4}(z)}{U_{\ell_0+6}(z)} \right|,$$
$$\eta_T(E;6) = \chi_\gamma(E;6) \left| \frac{U_{\ell_0+6}(z)}{U_{\ell_0+8}(z)} \right|.$$

Corollary 2 (Off-resonant two-segment penalty)**.** *Suppose $|z(E)| = \cosh \kappa > 1$. Then*

$$\eta_T(E;N) = \chi_\gamma(E;N) \frac{\sinh((\ell_0+N+1)\kappa)}{\sinh((\ell_0+N+3)\kappa)}.$$

If $\chi_\gamma(E;N) \to \chi_\gamma^\infty(E) > 0$, then

$$\lim_{N\to\infty} \eta_T(E;N) = \chi_\gamma^\infty(E) e^{-2\kappa} > 0.$$

Proof. Substitute the hyperbolic representation from Corollary 1. The limit follows by dividing numerator and denominator by $\exp((\ell_0+N+3)\kappa)$. □

Thus, within the homogeneous off-resonant model, the longer direction is suppressed relative to the shorter direction but is not electronically disconnected for finite N, finite κ, and nonzero attachment coefficients. In the propagating regime, by contrast,

$$\eta_T(E;N) = \chi_\gamma(E;N) \left| \frac{\sin((\ell_0+N+1)k)}{\sin((\ell_0+N+3)k)} \right|,$$

which need not vary monotonically with N. Candidate-specific evaluation is therefore required near resonances.

3.5 Admissible bridge orders

Definition 8 (Bridge-order feasibility set)**.** *At the predeclared comparison energy E^*, define*

$$\mathcal{N}_{\mathrm{adm}}(E^*) := \left\{ N \in 2\mathbb{Z}_{\geq 0} : \min\left(|T_x(E^*;N)|, |T_y(E^*;N)|\right) \geq t_{\mathrm{crit}} \right\}.$$

Proposition 5 (Two-direction coupling criterion)**.** *If*

$$N \in \mathcal{N}_{\mathrm{adm}}(E^*),$$

then

$$T_x(E^*;N) T_y(E^*;N) \neq 0.$$

Consequently, the reduced rectangular Bloch Hamiltonian has nonzero dispersion in both in-plane directions.

Proof. Membership in $\mathcal{N}_{\mathrm{adm}}(E^*)$ implies

$$|T_x(E^*;N)| \geq t_{\mathrm{crit}} > 0, \qquad |T_y(E^*;N)| \geq t_{\mathrm{crit}} > 0.$$

Their product is therefore nonzero. The two-direction dispersion result then follows from the rectangular Bloch model established in the main article. □

Remark 4 (Prospective use)**.** *The set $\mathcal{N}_{\mathrm{adm}}(E^*)$ shall be calculated before candidate selection. Values of N for which an attachment-site node, bridge antiresonance, excessive off-resonant decay, or uncertainty interval places either directional coupling below t_{crit} shall be excluded prospectively rather than rationalized after hydrogen-evolution testing.*

4 Mass-Normalized Density Calculations

The geometric density of a periodic network and its density per unit mass are distinct quantities. Shorter translation lengths increase the number of nodes per unit area, but they also increase the mass per unit area in the same proportion. Mass normalization must therefore be performed from the complete primitive-cell composition rather than inferred from lattice compactness alone.

4.1 Primitive-cell mass accounting

Definition 9 (Residue molar masses)**.** *Let*

$$\mathcal{M}_{\mathrm{Ch}}^{\mathrm{res}}$$

denote the molar mass of one 3, 6, 9, 12*-substituted chrysene node after network-forming reactions have occurred. Let*

$$\mathcal{M}_B^{(N),\mathrm{res}}, \qquad \mathcal{M}_B^{(N+2),\mathrm{res}}$$

denote the corresponding residue molar masses of the two directional crossbars. A primitive cell of $\mathfrak{R}_N$ contains one node and one representative of each undirected edge orbit. Its dry, unconditioned molar mass is therefore

$$\mathcal{M}_{\mathrm{cell}}^{(0)}(N) = \mathcal{M}_{\mathrm{Ch}}^{\mathrm{res}} + \mathcal{M}_B^{(N),\mathrm{res}} + \mathcal{M}_B^{(N+2),\mathrm{res}}.$$

All molar masses are expressed in $\mathrm{g\,mol^{-1}}$ *of primitive cells.*

Although each node has four incident crossbars in the infinite graph, every undirected edge is shared by two neighboring nodes. Consequently,

$$\frac{1}{2}\deg(v) = \frac{1}{2}(4) = 2$$

crossbars are assigned to each node, in agreement with the two edge orbits in the quotient graph.

If precursor rather than residue masses are used, the primitive-cell mass must include all network-forming losses.

Definition 10 (Precursor accounting convention)**.** *Let $\mathcal{M}_{\mathrm{Ch}}^{\mathrm{pre}}$ and $\mathcal{M}_B^{(m),\mathrm{pre}}$ denote precursor molar masses. Let $\mathcal{L}$ be the set of molecular fragments eliminated during network formation, and let $\nu_r(N)$ be the number of fragments of type $r \in \mathcal{L}$ eliminated per primitive cell. Then*

$$\mathcal{M}_{\mathrm{cell}}^{(0)}(N) = \mathcal{M}_{\mathrm{Ch}}^{\mathrm{pre}} + \mathcal{M}_B^{(N),\mathrm{pre}} + \mathcal{M}_B^{(N+2),\mathrm{pre}} - \sum_{r\in\mathcal{L}} \nu_r(N)\mathcal{M}_r^{\mathrm{loss}}.$$

The precursor and residue conventions are equivalent only when every leaving-group stoichiometry is included exactly once.

Metal occupancy, counterions, retained solvent, and other non-framework species modify the experimentally relevant mass. Write

$$\mathcal{M}_{\mathrm{cell}}(N) = \mathcal{M}_{\mathrm{cell}}^{(0)}(N) + \theta_M\mathcal{M}_M + \sum_{q\in Q}\theta_q\mathcal{M}_q,$$

where θ_M is the number of metal ions per primitive cell, $\mathcal{M}_M$ is the metal molar mass, and θ_q and $\mathcal{M}_q$ describe counterions, solvent, or other retained species. Every reported mass-normalized quantity shall state whether it uses the dry framework mass or the experimentally measured conditioned mass.

4.2 Areal, volumetric, and mass-normalized densities

Recall that the primitive-cell area is

$$A_N = a_N b_{N+2}.$$

If adjacent layers are separated by $c_N > 0$, the corresponding three-dimensional cell volume is

$$V_N = A_N c_N.$$

Definition 11 (Geometric densities)**.** *The node densities per unit area and volume are*

$$\rho_V^{(A)}(N) = \frac{1}{A_N}, \qquad \rho_V^{(V)}(N) = \frac{1}{V_N}.$$

Because there are two crossbars per primitive cell,

$$\rho_E^{(A)}(N) = \frac{2}{A_N}, \qquad \rho_E^{(V)}(N) = \frac{2}{V_N}.$$

The corresponding mass densities are

$$\sigma_m(N) = \frac{\mathcal{M}_{\mathrm{cell}}(N)}{N_{\mathrm{A}}A_N}$$

and

$$\rho_m(N) = \frac{\mathcal{M}_{\mathrm{cell}}(N)}{N_{\mathrm{A}} V_N},$$

where N_{A} is the Avogadro constant.

Proposition 6 (Cancellation of the geometric cell size)**.** *The numbers of nodes and crossbars per unit mass are*

$$n_V^{(m)}(N) = \frac{\rho_V^{(A)}(N)}{\sigma_m(N)} = \frac{N_{\mathrm{A}}}{\mathcal{M}_{\mathrm{cell}}(N)}$$

and

$$n_E^{(m)}(N) = \frac{\rho_E^{(A)}(N)}{\sigma_m(N)} = \frac{2N_{\mathrm{A}}}{\mathcal{M}_{\mathrm{cell}}(N)}.$$

The same expressions follow from the volumetric densities. Hence the translation lengths a_N, b_{N+2}, and c_N cancel under mass normalization.

Proof. Direct substitution gives

$$\frac{A_N^{-1}}{\mathcal{M}_{\mathrm{cell}}/(N_{\mathrm{A}} A_N)} = \frac{N_{\mathrm{A}}}{\mathcal{M}_{\mathrm{cell}}}.$$

Multiplication of the numerator by two gives the crossbar result. Replacing A_N by V_N proves the volumetric statement. □

Remark 5 (Meaning of compactness)**.** *A smaller A_N increases both node density and framework mass per unit area. It may improve optical depth, inter-node distance, catalyst proximity, or transport per unit area, but it does not by itself increase the number of nodes per gram. A mass-normalized advantage must arise from primitive-cell composition or from improved per-node photophysical performance.*

It is often convenient to express site densities in molar rather than number-count units. If a primitive cell contains ν_q sites of type q, define

$$C_q^{(m)}(N) := \frac{\nu_q}{\mathcal{M}_{\mathrm{cell}}(N)} \qquad \left[\text{mol of sites g}^{-1}\right].$$

In particular,

$$C_V^{(m)}(N) = \frac{1}{\mathcal{M}_{\mathrm{cell}}(N)}, \qquad C_E^{(m)}(N) = \frac{2}{\mathcal{M}_{\mathrm{cell}}(N)}.$$

4.3 Dependence on bridge order

Assume for this subsection that each added effective bridge segment contributes a residue molar mass $\Delta\mathcal{M}_B > 0$, while the reference crossbar has residue molar mass $\mathcal{M}_B^{(0),\mathrm{res}}$. Then

$$\mathcal{M}_B^{(m),\mathrm{res}} = \mathcal{M}_B^{(0),\mathrm{res}} + m\Delta\mathcal{M}_B.$$

Consequently,

$$\mathcal{M}_{\mathrm{cell}}^{(0)}(N) = \mathcal{M}_0 + (2N+2)\Delta\mathcal{M}_B,$$

where

$$\mathcal{M}_0 := \mathcal{M}_{\mathrm{Ch}}^{\mathrm{res}} + 2\mathcal{M}_B^{(0),\mathrm{res}}.$$

Proposition 7 (Node-density monotonicity)**.** *If $\Delta\mathcal{M}_B > 0$, then*

$$C_V^{(m)}(N) = \frac{1}{\mathcal{M}_0 + (2N+2)\Delta\mathcal{M}_B}$$

is strictly decreasing on $2\mathbb{Z}_{\geq 0}$.

Proof. For every admissible N,

$$\mathcal{M}_{\mathrm{cell}}^{(0)}(N+2) - \mathcal{M}_{\mathrm{cell}}^{(0)}(N) = 4\Delta\mathcal{M}_B > 0.$$

Taking positive reciprocals reverses the inequality. □

The number of added effective segments per primitive cell is

$$\nu_{\mathrm{seg}}(N) = N + (N+2) = 2N + 2.$$

Its mass-normalized molar density is therefore

$$C_{\mathrm{seg}}^{(m)}(N) = \frac{2N+2}{\mathcal{M}_0 + (2N+2)\Delta\mathcal{M}_B}.$$

Proposition 8 (Segment-density saturation)**.** *The quantity $C_{\mathrm{seg}}^{(m)}(N)$ is strictly increasing when $\mathcal{M}_0 > 0$, but satisfies*

$$\lim_{N\to\infty} C_{\mathrm{seg}}^{(m)}(N) = \frac{1}{\Delta\mathcal{M}_B}.$$

Proof. Let $x = 2N + 2$ and define

$$f(x) = \frac{x}{\mathcal{M}_0 + x\Delta\mathcal{M}_B}.$$

Then

$$f'(x) = \frac{\mathcal{M}_0}{(\mathcal{M}_0 + x\Delta\mathcal{M}_B)^2} > 0.$$

Dividing the numerator and denominator by x gives the stated limit. □

Thus, increasing N increases the number of bridge segments per gram but decreases the number of complete chrysene nodes per gram. Neither trend alone determines photocatalytic performance.

4.4 Mass-normalized optical and hydrogen rates

Let

$$\dot{n}_{\gamma,\mathrm{cell}}^{\mathrm{abs}}(N)$$

denote the absorbed-photon rate expressed in moles of absorbed photons per mole of primitive cells per hour. The corresponding mass-normalized rate is

$$\mathcal{A}_N^{(m)} = \frac{\dot{n}_{\gamma,\mathrm{cell}}^{\mathrm{abs}}(N)}{\mathcal{M}_{\mathrm{cell}}(N)} \qquad \left[\mathrm{mol}_\gamma\ \mathrm{g}^{-1}\ \mathrm{h}^{-1}\right].$$

The rate lower bound from the main article may therefore be written as

$$R_{\mathfrak{R}_N}^{\mathrm{LB}} = \frac{1}{2}\frac{\dot{n}_{\gamma,\mathrm{cell}}^{\mathrm{abs}}(N)}{\mathcal{M}_{\mathrm{cell}}(N)}\underline{\Phi}_{\mathrm{CS},N}\underline{\Phi}_{\mathrm{tr},N}\underline{\Phi}_{\mathrm{inj},N}\underline{\eta}_{\mathrm{Pt},N}.$$

Corollary 3 (Inactive-mass penalty)**.** *Suppose an added species increases the primitive-cell molar mass by* $\Delta\mathcal{M} > 0$ *but leaves the per-cell absorbed-photon rate and all quantum-yield factors unchanged. Then*

$$\frac{R_{\mathfrak{R}_N,\mathrm{new}}^{\mathrm{LB}}}{R_{\mathfrak{R}_N,\mathrm{old}}^{\mathrm{LB}}} = \frac{\mathcal{M}_{\mathrm{cell}}}{\mathcal{M}_{\mathrm{cell}} + \Delta\mathcal{M}} < 1.$$

The hypothesis of unchanged photophysical factors is essential. A metal, counterion, or substituent may increase the cell mass while also changing absorption, charge separation, transport, or injection. Such a conditioned system must be evaluated from the complete rate expression rather than from mass alone.

4.5 Comparison with another periodic material

Let a benchmark material X contain $\nu_{q,X}$ objects of type q per primitive cell and have primitive-cell molar mass $\mathcal{M}_{\mathrm{cell},X}$. Then

$$\frac{C_{q,\mathfrak{R}_N}^{(m)}}{C_{q,X}^{(m)}} = \frac{\nu_{q,\mathfrak{R}_N}}{\nu_{q,X}}\frac{\mathcal{M}_{\mathrm{cell},X}}{\mathcal{M}_{\mathrm{cell}}(N)}.$$

This comparison requires only verified stoichiometric cell contents and molar masses; it does not require transfer of the benchmark Hamiltonian, rate, or quantum yield.

Remark 6 (Reporting requirement)**.** *Every mass-normalized calculation shall report:*

1. *the empirical formula assigned to the primitive cell;*
2. *the node and directional crossbar counts;*
3. *the condensation fragments removed;*
4. *metal, counterion, and solvent occupancies;*
5. *the resulting* $\mathcal{M}_{\mathrm{cell}}(N)$*; and*
6. *whether the reported mass is theoretical dry mass or experimentally measured sample mass.*

Without these quantities, a comparison in $\mathrm{mol\,g^{-1}\,h^{-1}}$ *is not compositionally reproducible.*

5 Uncertainty Propagation Through the Rate Lower Bound

The hydrogen-evolution feasibility criterion depends on a product of quantities obtained from optical measurements, electronic-structure calculations, kinetic models, catalyst-access estimates, and assay calibration. Treating the constituent lower bounds as independent point estimates would generally overstate the confidence assigned to the final rate. This section defines deterministic and probabilistic procedures for propagating their joint uncertainty.

5.1 Product representation

Definition 12 (Rate-factor vector)**.** *For a fixed candidate* $\mathfrak{R}_N$*, define*

$$\mathbf{X}_N := \begin{pmatrix} X_{1,N} \\ X_{2,N} \\ X_{3,N} \\ X_{4,N} \\ X_{5,N} \end{pmatrix} := \begin{pmatrix} \mathcal{A}_N \\ \Phi_{\mathrm{CS},N} \\ \Phi_{\mathrm{tr},N} \\ \Phi_{\mathrm{inj},N} \\ \eta_{\mathrm{Pt},N} \end{pmatrix}.$$

Here

$$\mathcal{A}_N > 0$$

is the mass-normalized absorbed-photon rate, while

$$0 \le \Phi_{\mathrm{CS},N}, \Phi_{\mathrm{tr},N}, \Phi_{\mathrm{inj},N}, \eta_{\mathrm{Pt},N} \le 1.$$

Define

$$g(\mathbf{x}) := \frac{1}{2}\prod_{i=1}^{5} x_i.$$

The model-based hydrogen-evolution rate is

$$R_{\mathfrak{R}_N} = g(\mathbf{X}_N).$$

The factor $1/2$ accounts for the two-electron stoichiometry of molecular hydrogen. Uncertainty in photon absorption carries the physical units of the rate, whereas the remaining factors are dimensionless branching, transport, or utilization fractions.

Definition 13 (Uncertainty set)**.** *Let*

$$\mathcal{U}_N \subseteq \mathbb{R}_{>0} \times [0,1]^4$$

denote the admissible uncertainty set for $\mathbf{X}_N$*. The robust*

rate lower bound is

$$R^{\mathrm{rob}}_{\mathfrak{R}_N} := \inf_{\mathbf{x}\in\mathcal{U}_N} g(\mathbf{x}).$$

The set $\mathcal{U}_N$ may be deterministic, probabilistic, or constructed from a calibrated combination of computational and experimental uncertainties.

5.2 Deterministic interval propagation

Suppose first that

$$\mathcal{U}_N = \prod_{i=1}^{5} [\underline{x}_{i,N}, \overline{x}_{i,N}]$$

is a rectangular uncertainty set satisfying

$$0 \le \underline{x}_{i,N} \le \overline{x}_{i,N}.$$

Proposition 9 (Exact lower bound on a rectangular set)**.** *For the rectangular uncertainty set above,*

$$R^{\mathrm{rob}}_{\mathfrak{R}_N} = \frac{1}{2} \prod_{i=1}^{5} \underline{x}_{i,N}.$$

Proof. For every i,

$$\frac{\partial g}{\partial x_i} = \frac{1}{2} \prod_{\substack{j=1 \\ j\neq i}}^{5} x_j \ge 0$$

on $\mathbb{R}^5_{\ge 0}$. Hence g is coordinatewise nondecreasing. Its minimum over the rectangular set is attained at its lower corner

$$\underline{\mathbf{x}}_N = (\underline{x}_{1,N}, \dots, \underline{x}_{5,N})^{\mathsf{T}}.$$

□

Accordingly,

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} = \frac{1}{2} \underline{\mathcal{A}}_N \underline{\Phi}_{\mathrm{CS},N} \underline{\Phi}_{\mathrm{tr},N} \underline{\Phi}_{\mathrm{inj},N} \underline{\eta}_{\mathrm{Pt},N}.$$

Corollary 4 (Zero-factor rule)**.** *If any constituent lower bound is zero, then*

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

The candidate cannot be certified as detectably feasible by the product lower bound, irrespective of the remaining point estimates.

This rule is intentionally conservative. An unresolved factor cannot be replaced by its mean or best-fit value merely because the other factors are well characterized.

For a nonrectangular uncertainty set, the lower corner need not belong to $\mathcal{U}_N$. The correct robust value remains

$$\inf_{\mathbf{x}\in\mathcal{U}_N} g(\mathbf{x}),$$

which may be greater than the rectangular result if physical constraints exclude simultaneous attainment of all marginal minima.

5.3 Simultaneous probabilistic coverage

Individual one-sided confidence limits do not automatically provide the same coverage for their product.

Proposition 10 (Propagation of a simultaneous confidence event)**.** *Suppose that random lower bounds $\underline{X}_{i,N}$ satisfy*

$$\mathbb{P}\left[X_{i,N} \ge \underline{X}_{i,N} \text{ for every } i = 1, \dots, 5\right] \ge 1 - \alpha.$$

Then

$$\mathbb{P}\left[R_{\mathfrak{R}_N} \ge \frac{1}{2} \prod_{i=1}^{5} \underline{X}_{i,N}\right] \ge 1 - \alpha.$$

Proof. On the simultaneous event

$$\bigcap_{i=1}^{5} \{X_{i,N} \ge \underline{X}_{i,N}\},$$

coordinatewise monotonicity gives

$$g(\mathbf{X}_N) \ge g(\underline{\mathbf{X}}_N).$$

The probability of this event is at least $1 - \alpha$. □

If only marginal lower bounds are available, simultaneous coverage may be constructed without assuming independence.

Corollary 5 (Bonferroni construction)**.** *Suppose*

$$\mathbb{P}\left[X_{i,N} < \underline{X}_{i,N}\right] \le \alpha_i$$

for $i = 1, \dots, 5$, where

$$\sum_{i=1}^{5} \alpha_i \le \alpha.$$

Then the product lower bound has coverage at least $1 - \alpha$.

Proof. By the union bound,

$$\mathbb{P}\left[\bigcup_{i=1}^{5} \{X_{i,N} < \underline{X}_{i,N}\}\right] \le \sum_{i=1}^{5} \alpha_i \le \alpha.$$

The complementary simultaneous event therefore has proba-

bility at least $1-\alpha$, and Proposition 10 applies. □

An equal allocation uses

$$\alpha_i = \frac{\alpha}{5}.$$

This construction is conservative but remains valid when the factors are correlated. If independence is established, equal marginal coverage

$$1-\alpha_i = (1-\alpha)^{1/5}$$

gives exact joint coverage $1-\alpha$. Independence shall not be assumed merely because the factors have different physical names.

5.4 Logarithmic sensitivity and covariance

When all factors are strictly positive, define

$$Y_{i,N} := \log X_{i,N}.$$

Then

$$\log R_{\mathfrak{R}_N} = -\log 2 + \sum_{i=1}^{5} Y_{i,N}.$$

Proposition 11 (Unit logarithmic elasticities)**.** *For every* $i = 1, \dots, 5$*,*

$$\frac{\partial \log R_{\mathfrak{R}_N}}{\partial \log X_{i,N}} = 1.$$

Thus a small relative perturbation in any one factor produces the same first-order relative perturbation in the rate when the other factors are fixed.

Proof. Differentiate

$$\log R_{\mathfrak{R}_N} = -\log 2 + \sum_{j=1}^{5} \log X_{j,N}$$

with respect to $\log X_{i,N}$. □

Equal elasticity does not imply equal contribution to uncertainty. Let

$$\boldsymbol{\mu}_Y = \mathbb{E}[\mathbf{Y}_N], \qquad \boldsymbol{\Sigma}_Y = \mathrm{Cov}(\mathbf{Y}_N).$$

Then

$$\mathrm{Var}\left(\log R_{\mathfrak{R}_N}\right) = \mathbf{1}^{\mathsf{T}} \boldsymbol{\Sigma}_Y \mathbf{1},$$

where

$$\mathbf{1} = (1,1,1,1,1)^{\mathsf{T}}.$$

Equivalently,

$$\mathrm{Var}\left(\log R_{\mathfrak{R}_N}\right) = \sum_{i=1}^{5} \mathrm{Var}(Y_{i,N}) + 2 \sum_{1 \le i < j \le 5} \mathrm{Cov}(Y_{i,N}, Y_{j,N}).$$

Positive covariance increases the rate uncertainty; negative covariance may partially reduce it. Covariance terms must therefore be retained when two factors are derived from common spectra, shared kinetic fits, common geometry calculations, or the same experimental replicates.

Corollary 6 (Mass-normalization elasticity)**.** *If*

$$\mathcal{A}_N = \frac{\dot{n}^{\mathrm{abs}}_{\gamma,\mathrm{cell}}(N)}{\mathcal{M}_{\mathrm{cell}}(N)},$$

then

$$\log R_{\mathfrak{R}_N} = -\log 2 + \log \dot{n}^{\mathrm{abs}}_{\gamma,\mathrm{cell}} - \log \mathcal{M}_{\mathrm{cell}} + \sum_{i=2}^{5} \log X_{i,N}.$$

Consequently,

$$\frac{\partial \log R_{\mathfrak{R}_N}}{\partial \log \mathcal{M}_{\mathrm{cell}}} = -1$$

when all per-cell photophysical factors are held fixed.

5.5 Joint lognormal approximation

A closed-form probabilistic lower bound is available under a joint lognormal approximation.

Proposition 12 (Lognormal rate quantile)**.** *Suppose*

$$\mathbf{Y}_N = \log \mathbf{X}_N \sim \mathcal{N}\left(\boldsymbol{\mu}_Y, \boldsymbol{\Sigma}_Y\right).$$

Set

$$\mu_R = -\log 2 + \mathbf{1}^{\mathsf{T}} \boldsymbol{\mu}_Y$$

and

$$\sigma_R^2 = \mathbf{1}^{\mathsf{T}} \boldsymbol{\Sigma}_Y \mathbf{1}.$$

Then a one-sided $(1-\alpha)$*-level lower confidence bound is*

$$R^{\mathrm{LB}}_{\mathfrak{R}_N,\alpha} = \exp\left(\mu_R - z_{1-\alpha}\sigma_R\right),$$

where $z_{1-\alpha}$ *is the* $(1-\alpha)$*-quantile of the standard normal distribution.*

Proof. The linear combination

$$\log R_{\mathfrak{R}_N} = -\log 2 + \mathbf{1}^{\mathsf{T}} \mathbf{Y}_N$$

is normally distributed with mean μ_R and variance σ_R^2. Its lower α-quantile is $\mu_R - z_{1-\alpha}\sigma_R$. Exponentiation gives the result. □

The lognormal expression shall be used only when the positivity, tail behavior, and covariance model are supported by diagnostics. It is inappropriate for factors having substantial probability at zero, strong censoring, unidentified multimodality,

or model-selection uncertainty.

5.6 Bootstrap and Monte Carlo propagation

When the joint distribution is non-Gaussian, uncertainty shall be propagated through the complete calculation rather than by independently sampling marginal factors.

Definition 14 (Joint resampling procedure)**.** *For bootstrap or posterior draws*

$$\mathbf{X}_N^{(b)} = \left(\mathcal{A}_N^{(b)}, \Phi_{\mathrm{CS},N}^{(b)}, \Phi_{\mathrm{tr},N}^{(b)}, \Phi_{\mathrm{inj},N}^{(b)}, \eta_{\mathrm{Pt},N}^{(b)}\right), \qquad b = 1, \ldots, B,$$

define

$$R_N^{(b)} = \frac{1}{2} \prod_{i=1}^{5} X_{i,N}^{(b)}.$$

The empirical lower bound is

$$R_{\mathfrak{R}_N,\alpha}^{\mathrm{LB}} = \widehat{Q}_\alpha \left(R_N^{(1)}, \ldots, R_N^{(B)}\right),$$

where $\widehat{Q}_\alpha$ is a prospectively specified lower-quantile estimator.

Each draw shall preserve shared sources of uncertainty. For example, a single geometry draw should be propagated jointly into electronic coupling, redox alignment, carrier transport, and catalyst distance. Likewise, a spectroscopic bootstrap replicate should be propagated jointly into every factor estimated from the same transient data. Resampling the five final factors independently destroys these dependencies and is not permitted unless independence has been demonstrated.

The calculation shall distinguish:

1. *parameter uncertainty*, arising from finite data or fitted model parameters;
2. *measurement uncertainty*, arising from instrumental noise, calibration, sample preparation, and replicate variation;
3. *model-form uncertainty*, arising from alternative Hamiltonians, kinetic models, exchange–correlation functionals, or transport approximations; and
4. *candidate heterogeneity*, arising from defects, particle sizes, stacking states, Pt distributions, and batch variation.

Model-form alternatives shall be sampled or bounded explicitly. Selecting the model that produces the largest lower bound after observing the hydrogen-evolution result is not admissible.

5.7 Construction of constituent bounds

Computational prediction intervals shall be calibrated on data not used for model fitting or candidate selection. If nominal prediction intervals fail their prospectively specified empirical-coverage criterion, they shall be recalibrated or widened before candidate certification. An uncalibrated model standard deviation is not a substitute for a validated prediction interval.

Table 2: Principal uncertainty sources entering the rate lower bound.

Factor	Principal uncertainty sources
$\mathcal{A}_N$	Incident photon flux, spectral calibration, absorption model, sample mass, optical scattering, and wavelength integration.
$\Phi_{\mathrm{CS},N}$	Excited-state assignment, redox potentials, E_{00}, kinetic fitting, reorganization model, and competing relaxation pathways.
$\Phi_{\mathrm{tr},N}$	Directional coupling, mobility or diffusion model, lifetime, defects, domain size, anisotropy, and catalyst-distance distribution.
$\Phi_{\mathrm{inj},N}$	Interfacial coupling, Pt electronic state, transfer-rate model, surface coverage, and competing electron traps.
$\eta_{\mathrm{Pt},N}$	Pt loading, dispersion, accessibility, photodeposition variability, and fraction of Pt sites producing hydrogen.
R_{LOQ}	Blank variance, calibration curve, detector drift, gas leakage, integration procedure, and replicate design.

5.8 Uncertainty in the assay threshold

The limit of quantification is itself estimated. Let

$$\overline{R}_{\mathrm{LOQ},\alpha}$$

denote a one-sided upper confidence bound on the background-corrected quantification threshold.

Definition 15 (Robust detectability margin)**.** *The robust detectability margin is*

$$\mathscr{M}_{N,\alpha} := R_{\mathfrak{R}_N,\alpha}^{\mathrm{LB}} - \overline{R}_{\mathrm{LOQ},\alpha}.$$

A candidate is prospectively certified only if

$$\mathscr{M}_{N,\alpha} > 0.$$

If R_{LOQ} is fixed by a validated assay procedure and treated as nonrandom, then

$$\overline{R}_{\mathrm{LOQ},\alpha} = R_{\mathrm{LOQ}}.$$

For the observed experiment, let

$$R_{\mathrm{sig},N}$$

denote the illuminated material-plus-Pt signal and $R_{\mathrm{bg},N}$ the applicable background. A conservative background-corrected lower bound is

$$\underline{R}_{\mathrm{net},N} = \underline{R}_{\mathrm{sig},N} - \overline{R}_{\mathrm{bg},N}.$$

The experimental success criterion is

$$\underline{R}_{\mathrm{net},N} > \overline{R}_{\mathrm{LOQ},\alpha},$$

together with prospectively specified comparisons against the dark, no-material, and no-Pt controls.

5.9 Multiplicity across prospective candidates

Suppose five candidates are tested:

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

If candidate q is assigned false-certification probability α_q, family-wise control at level α_{F} is obtained by requiring

$$\sum_{q=1}^{5} \alpha_q \le \alpha_{\mathrm{F}}.$$

An equal Bonferroni allocation gives

$$\alpha_q = \frac{\alpha_{\mathrm{F}}}{5}.$$

Alternatively, one candidate may be declared the primary prospective test and the remaining candidates designated exploratory before measurements are unblinded. The multiplicity procedure shall be stated in the experimental protocol and shall not be selected after observing which candidate performs best.

Remark 7 (Certification rule)**.** *The uncertainty analysis has two distinct outputs:*

1. *a pre-experimental predictive lower bound used to select candidates; and*
2. *a post-measurement lower confidence bound used to determine whether a candidate produced a detectable hydrogen signal.*

The former does not establish experimental activity, and the latter does not validate every mechanistic factor in the predictive model. Phase I feasibility requires both prospective model evaluation and controlled experimental confirmation.

6 Metal-Ion Perturbation Calculations

Metal incorporation is treated as a bounded perturbation of the unconditioned rectangular chrysene network. No metal is assumed *a priori* to improve hydrogen evolution. A metal may shift frontier energies, alter stacking geometry, introduce charge-transfer states, or provide an electron-relay pathway; it may also localize carriers, increase the primitive-cell mass, or accelerate nonradiative decay. Experimental studies of isostructural metal-containing COFs likewise show that metal identity can alter charge-carrier dynamics without guaranteeing improved photocatalytic performance [CWM+21].

6.1 Metal-conditioned state specification

Definition 16 (Metal-conditioning state)**.** *A metal-conditioned candidate is indexed by*

$$\mathfrak{m} = (M, q_M, S_M, \mathbf{R}_M, C_M, \mathbf{d}_{M-\pi}, \boldsymbol{\theta}_M, \mathcal{I}_M, \varepsilon_{\mathrm{env}}),$$

where:

1. *M is the metal identity;*
2. *q_M is its formal oxidation state;*
3. *S_M is its spin state;*
4. *$\mathbf{R}_M$ is its position in the chrysene stack;*
5. *C_M is its coordination environment;*
6. *$\mathbf{d}_{M-\pi}$ contains the metal–π distances to adjacent chrysene planes;*
7. *$\boldsymbol{\theta}_M$ contains stack slip, twist, and local angular variables;*
8. *$\mathcal{I}_M$ specifies counterions and their positions; and*
9. *$\varepsilon_{\mathrm{env}}$ represents the dielectric and chemical environment.*

Two candidates having the same metal identity but different oxidation or spin states are treated as distinct conditioning states.

For the bounded Phase I transfer test, the admissible set

$$\mathscr{M}_{\mathrm{I}} = \{\mathfrak{m}_1, \ldots, \mathfrak{m}_r\}$$

shall be finite and fixed before prospective measurements. It shall not represent an unrestricted search over all metals, oxidation states, spin states, and geometries.

Remark 8 (Distinct metal roles)**.** *Mg is treated initially as a comparatively redox-inert electrostatic and structural conditioner. It is not assumed to catalyze proton reduction. Transition metals such as Fe, Co, Ni, Cu, or Mn may introduce redox-active or spin-active states, but may also create traps and nonradiative pathways. Platinum remains the terminal hydrogen-evolution cocatalyst unless an alternative catalytic role is independently established.*

6.2 Block Hamiltonian and Schur reduction

Let $\mathcal{H}_{\mathfrak{R}}$ be the effective frontier-state space of the unconditioned chrysene network, and let $\mathcal{H}_M$ be the metal-centered state space associated with $\mathfrak{m}$.

Definition 17 (Metal-conditioned Hamiltonian)**.** *Let*

$$H_{\mathfrak{R}} : \mathcal{H}_{\mathfrak{R}} \longrightarrow \mathcal{H}_{\mathfrak{R}}$$

be the unconditioned network Hamiltonian,

$$H_M(\mathfrak{m}) : \mathcal{H}_M \longrightarrow \mathcal{H}_M$$

the metal-subspace Hamiltonian, and

$$V_M(\mathfrak{m}) : \mathcal{H}_{\mathfrak{R}} \longrightarrow \mathcal{H}_M$$

the network-to-metal coupling. Define

$$H_{\mathrm{tot}}(\mathfrak{m}) = \begin{pmatrix} H_{\mathfrak{R}} & V_M(\mathfrak{m})^\dagger \\ V_M(\mathfrak{m}) & H_M(\mathfrak{m}) \end{pmatrix}.$$

Proposition 13 (Metal self-energy)**.** *Suppose*

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

The projection of $(EI - H_{\mathrm{tot}}(\mathfrak{m}))^{-1}$ *onto* $\mathcal{H}_{\mathfrak{R}}$ *is*

$$G_{\mathfrak{R}}^{(\mathfrak{m})}(E) = \left[EI - H_{\mathfrak{R}} - \Sigma_M(E;\mathfrak{m})\right]^{-1},$$

where

$$\Sigma_M(E;\mathfrak{m}) = V_M(\mathfrak{m})^\dagger \left[EI - H_M(\mathfrak{m})\right]^{-1} V_M(\mathfrak{m}).$$

Proof. Apply the Schur-complement formula to $EI - H_{\mathrm{tot}}(\mathfrak{m})$, eliminating the metal-centered block. □

The operator Σ_M contains the metal-induced energetic shift, orbital mixing, and effective coupling between network states. It is energy-dependent and shall not generally be replaced by a constant empirical offset.

Proposition 14 (Off-resonant self-energy bound)**.** *Assume* $H_M(\mathfrak{m})$ *is Hermitian and define*

$$\Delta_M(E;\mathfrak{m}) := \mathrm{dist}\left(E, \mathrm{Spec}(H_M(\mathfrak{m}))\right).$$

If $\Delta_M(E;\mathfrak{m}) > 0$*, then*

$$\|\Sigma_M(E;\mathfrak{m})\| \le \frac{\|V_M(\mathfrak{m})\|^2}{\Delta_M(E;\mathfrak{m})}.$$

Proof. For a Hermitian operator,

$$\left\|(EI - H_M)^{-1}\right\| = \frac{1}{\mathrm{dist}(E, \mathrm{Spec}(H_M))}.$$

Submultiplicativity of the operator norm gives

$$\|\Sigma_M\| \le \|V_M^\dagger\| \left\|(EI - H_M)^{-1}\right\| \|V_M\|,$$

and $\|V_M^\dagger\| = \|V_M\|$. □

This bound distinguishes two limiting regimes. A weakly coupled, energetically distant metal state produces a bounded perturbation of order

$$O\left(\frac{\|V_M\|^2}{\Delta_M}\right).$$

A near-resonant metal state may strongly alter the network spectrum, but the perturbative approximation then becomes unreliable and the complete block Hamiltonian must be diagonalized.

6.3 Electrostatic and distance-dependent approximations

For a primarily electrostatic conditioner, define the potential

$$\phi_M(\mathbf{r}) = \frac{q_M e}{4\pi\varepsilon_0\varepsilon_{\mathrm{env}}|\mathbf{r} - \mathbf{R}_M|} + \phi_{\mathcal{I}_M}(\mathbf{r}),$$

where $\phi_{\mathcal{I}_M}$ is the counterion contribution. The first-order shift of a localized electronic state $|\varphi_i\rangle$ is

$$\delta\varepsilon_i^{\mathrm{el}} = -e \int |\varphi_i(\mathbf{r})|^2 \phi_M(\mathbf{r})\, d\mathbf{r}.$$

This point-charge expression is an initial screening approximation only. Polarization, charge transfer, coordination, and solvent response require an explicit electronic-structure calculation.

A phenomenological metal–π coupling may be written

$$\|V_M(d)\| = V_{M,0} \exp\left[-\beta_M(d - d_{M,0})\right], \qquad \beta_M > 0.$$

Consequently, uncertainty in the metal–π distance propagates exponentially into the coupling:

$$\frac{\partial \log \|V_M(d)\|}{\partial d} = -\beta_M.$$

Metal position and stack separation must therefore be included in the uncertainty analysis rather than fixed solely from an idealized geometry.

6.4 Single-level metal model and induced decay

A minimal redox-active model assigns one broadened metal state of energy ε_M and linewidth $\Gamma_M \ge 0$. Let $|v_M\rangle \in \mathcal{H}_{\mathfrak{R}}$ be its coupling vector. Then

$$\Sigma_M(E) = \frac{|v_M\rangle\langle v_M|}{E - \varepsilon_M + i\Gamma_M/2}.$$

Equivalently,

$$\Sigma_M(E) = |v_M\rangle\langle v_M| \, \frac{(E - \varepsilon_M) - i\Gamma_M/2}{(E - \varepsilon_M)^2 + (\Gamma_M/2)^2}.$$

For a normalized network state $|\psi\rangle$, define

$$\delta E_M(\psi; E) := \mathrm{Re}\,\langle\psi|\,\Sigma_M(E)\,|\psi\rangle$$

and

$$\Gamma_{\mathrm{ind}}(\psi; E) := -2\,\mathrm{Im}\,\langle\psi|\,\Sigma_M(E)\,|\psi\rangle\,.$$

The corresponding induced loss rate is

$$k_{\mathrm{ind}}(\psi; E) = \frac{\Gamma_{\mathrm{ind}}(\psi; E)}{\hbar}.$$

Proposition 15 (Shift–broadening tradeoff)**.** *For the single-level model,*

$$\delta E_M(\psi; E) = |\,\langle v_M|\psi|v_M|\psi\rangle\,|^2 \frac{E - \varepsilon_M}{(E-\varepsilon_M)^2 + (\Gamma_M/2)^2}$$

and

$$\Gamma_{\mathrm{ind}}(\psi; E) = |\,\langle v_M|\psi|v_M|\psi\rangle\,|^2 \frac{\Gamma_M}{(E-\varepsilon_M)^2 + (\Gamma_M/2)^2}.$$

Thus a metal state near resonance can produce a large energetic shift while simultaneously introducing substantial broadening and decay.

Proof. Take the real and imaginary parts of $\langle\psi|\,\Sigma_M(E)\,|\psi\rangle$. □

For multiple metal-centered states a, the self-energy becomes

$$\Sigma_M(E) = \sum_a \frac{|v_{M,a}\rangle\langle v_{M,a}|}{E - \varepsilon_{M,a} + i\Gamma_{M,a}/2},$$

with each state indexed by its orbital character, oxidation state, and spin multiplicity.

6.5 Perturbation of directional coupling

Let $H_{B,\alpha}$ denote the bridge or local node–bridge Hamiltonian in direction $\alpha \in \{x, y\}$. If the metal perturbs that subspace through $\Sigma_{M,\alpha}$, define

$$T_\alpha^{(\mathfrak{m})}(E) = \mathbf{v}_{L,\alpha}^\dagger \left[EI - H_{B,\alpha} - \Sigma_{M,\alpha}(E;\mathfrak{m})\right]^{-1} \mathbf{v}_{R,\alpha}.$$

Let

$$G_\alpha^{(0)}(E) = (EI - H_{B,\alpha})^{-1}$$

and

$$G_\alpha^{(\mathfrak{m})}(E) = \left[EI - H_{B,\alpha} - \Sigma_{M,\alpha}(E;\mathfrak{m})\right]^{-1}.$$

Lemma 16 (Resolvent perturbation identity)**.** *Whenever both resolvents exist,*

$$G_\alpha^{(\mathfrak{m})} - G_\alpha^{(0)} = G_\alpha^{(0)}\Sigma_{M,\alpha}G_\alpha^{(\mathfrak{m})}.$$

Proof. This is the second resolvent identity applied to $EI - H_{B,\alpha}$ and $EI - H_{B,\alpha} - \Sigma_{M,\alpha}$. □

Proposition 17 (Bound on coupling perturbation)**.** *Suppose*

$$\left\|G_\alpha^{(0)}(E)\right\|\,\left\|\Sigma_{M,\alpha}(E)\right\| < 1.$$

Then

$$\left\|G_\alpha^{(\mathfrak{m})}(E) - G_\alpha^{(0)}(E)\right\| \le \frac{\|G_\alpha^{(0)}(E)\|^2\|\Sigma_{M,\alpha}(E)\|}{1 - \|G_\alpha^{(0)}(E)\|\|\Sigma_{M,\alpha}(E)\|},$$

and

$$\left|T_\alpha^{(\mathfrak{m})}(E) - T_\alpha^{(0)}(E)\right| \le \delta T_{\alpha,M}(E),$$

where

$$\delta T_{\alpha,M}(E) := \|\mathbf{v}_{L,\alpha}\|\|\mathbf{v}_{R,\alpha}\|\frac{\|G_\alpha^{(0)}(E)\|^2\|\Sigma_{M,\alpha}(E)\|}{1 - \|G_\alpha^{(0)}(E)\|\|\Sigma_{M,\alpha}(E)\|}.$$

Proof. The assumed inequality permits the Neumann expansion

$$G_\alpha^{(\mathfrak{m})} = \left(I - G_\alpha^{(0)}\Sigma_{M,\alpha}\right)^{-1} G_\alpha^{(0)}.$$

Taking norms in Lemma 16 gives the resolvent bound. Applying the endpoint vectors gives the coupling bound. □

Corollary 7 (Sufficient preservation of two-direction coupling)**.** *If*

$$|T_\alpha^{(0)}(E^*)| - \delta T_{\alpha,M}(E^*) \ge t_{\mathrm{crit}}$$

for $\alpha = x, y$, then

$$\min_{\alpha\in\{x,y\}} |T_\alpha^{(\mathfrak{m})}(E^*)| \ge t_{\mathrm{crit}}.$$

This criterion certifies that metal conditioning does not destroy the minimum directional coupling. It does not require the metal to increase either coupling.

6.6 Energetic alignment under metal conditioning

Write

$$\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} = \Delta G_{\mathrm{CS}}^{(0)} + \delta_M^{\mathrm{CS}}$$

and

$$\Delta G_H^{(\mathfrak{m})} = \Delta G_H^{(0)} + \delta_M^H,$$

where δ_M^{CS} and δ_M^H contain metal-induced changes in excited-state, oxidation, reduction, solvation, and interfacial energies.

Suppose

$$|\delta_M^{\mathrm{CS}} - \widehat{\delta}_M^{\mathrm{CS}}| \le \epsilon_M^{\mathrm{CS}}$$

and

$$|\delta_M^H - \widehat{\delta}_M^H| \le \epsilon_M^H.$$

The robust energetic conditions are

$$\Delta G_{\mathrm{CS}}^{(0)} + \widehat{\delta}_M^{\mathrm{CS}} + \epsilon_M^{\mathrm{CS}} \le -\delta_{\mathrm{CS}}$$

and

$$\Delta G_H^{(0)} + \widehat{\delta}_M^H + \epsilon_M^H \le -\delta_H.$$

Remark 9 (No benefit from alignment alone)**.** *A favorable shift in ΔG_{CS} or ΔG_H does not establish improved activity. The same metal may decrease excited-state lifetime, directional coupling, transport length, or Pt injection. Energetic alignment is one factor in the complete rate product.*

6.7 Charge-separation benefit versus metal quenching

Let $k_s > 0$ denote the unconditioned productive charge-separation rate and let $k_\ell > 0$ denote the sum of competing unconditioned loss rates. Then

$$\Phi_{\mathrm{CS}}^{(0)} = \frac{k_s}{k_s + k_\ell}.$$

Suppose metal conditioning introduces a productive rate $k_{s,M} \ge 0$ and an additional quenching rate $k_{q,M} \ge 0$. The conditioned yield is

$$\Phi_{\mathrm{CS}}^{(\mathfrak{m})} = \frac{k_s + k_{s,M}}{k_s + k_{s,M} + k_\ell + k_{q,M}}.$$

Proposition 18 (Net charge-separation improvement criterion)**.** *The inequality*

$$\Phi_{\mathrm{CS}}^{(\mathfrak{m})} \ge \Phi_{\mathrm{CS}}^{(0)}$$

holds if and only if

$$k_{s,M} k_\ell \ge k_s k_{q,M}.$$

Proof. Because all denominators are positive,

$$\frac{k_s + k_{s,M}}{k_s + k_{s,M} + k_\ell + k_{q,M}} \ge \frac{k_s}{k_s + k_\ell}$$

is equivalent, after cross multiplication and cancellation, to

$$k_{s,M} k_\ell \ge k_s k_{q,M}.$$

□

Thus, the existence of a new metal-mediated charge-transfer pathway is not sufficient. Its productive contribution must outweigh the accompanying quenching relative to the baseline separation and loss rates.

A weaker admissibility requirement is

$$\underline{\Phi}_{\mathrm{CS}}^{(\mathfrak{m})} \ge \phi_{\mathrm{CS,min}},$$

even if the conditioned yield is lower than the unconditioned yield. Likewise, the conditioned excited-state lifetime must satisfy the transport requirement

$$L_{\mathrm{diff},\alpha}^{(\mathfrak{m})} = \sqrt{D_\alpha^{(\mathfrak{m})} \tau^{(\mathfrak{m})}} \ge d_{\mathrm{Pt},\alpha}^{(\mathfrak{m})}$$

in every direction needed for catalyst access.

6.8 Mass-normalized conditioned rate

Let the conditioned primitive-cell mass be

$$\mathcal{M}_{\mathrm{cell}}^{(\mathfrak{m})} = \mathcal{M}_{\mathrm{cell}}^{(0)} + \theta_M \mathcal{M}_M + \sum_{q \in Q} \theta_q \mathcal{M}_q.$$

The metal-conditioned rate lower bound is

$$R_{\mathfrak{R}_N}^{(\mathfrak{m}),\mathrm{LB}} = \frac{1}{2} \frac{\dot{n}_{\gamma,\mathrm{cell}}^{(\mathfrak{m}),\mathrm{abs}}}{\mathcal{M}_{\mathrm{cell}}^{(\mathfrak{m})}} \underline{\Phi}_{\mathrm{CS}}^{(\mathfrak{m})} \underline{\Phi}_{\mathrm{tr}}^{(\mathfrak{m})} \times \underline{\Phi}_{\mathrm{inj}}^{(\mathfrak{m})} \underline{\eta}_{\mathrm{Pt}}^{(\mathfrak{m})}.$$

If the unconditioned lower bound is positive, define the conditioned-gain ratio

$$\mathcal{G}_M := \frac{R_{\mathfrak{R}_N}^{(\mathfrak{m}),\mathrm{LB}}}{R_{\mathfrak{R}_N}^{(0),\mathrm{LB}}}.$$

A value $\mathcal{G}_M > 1$ indicates improvement only under the common normalization, illumination, uncertainty, and catalyst conventions used in both calculations. Phase I feasibility does not require $\mathcal{G}_M > 1$; it requires

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

6.9 Bounded calculation protocol

For each $\mathfrak{m} \in \mathscr{M}_{\mathrm{I}}$, the following quantities shall be recorded before experimental testing:

1. metal identity, oxidation state, spin state, counterions, and environmental conditions;
2. optimized metal–π distances, stack separation, slip, twist, and coordination geometry;
3. the metal-centered spectrum $\mathrm{Spec}(H_M(\mathfrak{m}))$;
4. the coupling operator $V_M(\mathfrak{m})$ and self-energy $\Sigma_M(E;\mathfrak{m})$;
5. conditioned directional couplings $T_x^{(\mathfrak{m})}(E^*)$ and $T_y^{(\mathfrak{m})}(E^*)$;

6. conditioned optical and redox quantities;
7. induced broadening, excited-state lifetime, and quenching-rate bounds;
8. conditioned primitive-cell mass and mass-normalized absorption; and
9. the simultaneous lower bound $R_{\mathfrak{R}_N}^{(\mathfrak{m}),\mathrm{LB}}$.

Definition 18 (Metal-conditioned certification)**.** *A metal-conditioned candidate is certified for prospective testing only if all of the following hold:*

$$\min\left\{|T_x^{(\mathfrak{m})}(E^*)|, |T_y^{(\mathfrak{m})}(E^*)|\right\} \geq t_{\mathrm{crit}},$$
$$\Delta G_{\mathrm{CS}}^{(\mathfrak{m})} \leq -\delta_{\mathrm{CS}}, \qquad \Delta G_H^{(\mathfrak{m})} \leq -\delta_H,$$
$$\underline{\Phi}_{\mathrm{CS}}^{(\mathfrak{m})} \geq \phi_{\mathrm{CS,min}}, \qquad \chi_{\mathrm{Pt}}^{(\mathfrak{m})} \leq 1,$$
$$R_{\mathfrak{R}_N}^{(\mathfrak{m}),\mathrm{LB}} > R_{\mathrm{LOQ}}.$$

Every inequality is evaluated with the uncertainty procedure of Section 5.

Remark 10 (Interpretive limitation)**.** *Metal conditioning expands the design space but does not repair a candidate that fails an unexamined physical requirement. A favorable calculated metal interaction cannot substitute for prospective measurements of absorption, charge separation, lifetime, transport, Pt accessibility, and hydrogen evolution. The bounded transfer test evaluates whether the lattice formalism and inverse-design workflow can represent and rank metal-conditioned candidates; it is not a separate unrestricted metal-photocatalyst discovery program.*

7 Reproducibility and Calculation Sequence

The calculations are reproducible only if the molecular structure, physical state, numerical method, parameter provenance, uncertainty construction, and decision thresholds are fixed together. A chemical drawing or final rate estimate alone is not a complete computational record.

Definition 19 (Reproducibility bundle)**.** *For each candidate $\mathfrak{R}_N^{(q)}$, define its reproducibility bundle by*

$$\mathscr{B}_N^{(q)} = \left(\mathscr{I}_N^{(q)}, \mathscr{G}_N^{(q)}, \mathscr{E}_N^{(q)}, \mathscr{U}_N^{(q)}, \mathscr{D}_N^{(q)}\right),$$

where:

1. *$\mathscr{I}_N^{(q)}$ is the chemical and topological identification record;*
2. *$\mathscr{G}_N^{(q)}$ is the geometry and environmental record;*
3. *$\mathscr{E}_N^{(q)}$ is the electronic-structure and kinetic calculation record;*
4. *$\mathscr{U}_N^{(q)}$ is the uncertainty and calibration record; and*
5. *$\mathscr{D}_N^{(q)}$ is the prospective decision record.*

The identification record shall contain the node structure, attachment-site labels, crossbar structures, bridge order N, periodic connection rules, metal-conditioning state if present, empirical primitive-cell formula, and a unique candidate identifier. Machine-readable structures shall be stored as appropriate molecular and periodic-coordinate files.

The geometry record shall contain the initial and optimized coordinates, unit-cell parameters, stacking relation, metal–π distances, counterions, charge, spin multiplicity, dielectric or solvent model, and all geometry constraints. Distinct conformers, oxidation states, or spin states shall receive distinct identifiers.

7.1 Prospective calculation sequence

For every candidate, the following sequence shall be executed in the stated order.

(C1) Freeze the candidate definition. Record

$$N, \qquad \mathrm{C3}-\mathrm{C9}, \qquad \mathrm{C12}-\mathrm{C6}, \qquad \mathfrak{m},$$

together with the node, bridge, stacking, and environmental specifications. The candidate identifier is fixed before property calculations are examined.

(C2) Optimize and verify the geometry. Determine

$$a_N, \qquad b_{N+2}, \qquad c_N$$

where applicable. Verify preservation of the intended connectivity and reject structures exhibiting bond rearrangement, lattice collapse, or loss of the declared topology.

(C3) Construct the bridge Hamiltonians. Calculate

$$H_B^{(N)}, \qquad H_B^{(N+2)},$$

and the attachment vectors

$$\mathbf{v}_3, \quad \mathbf{v}_9, \quad \mathbf{v}_{12}, \quad \mathbf{v}_6.$$

Evaluate

$$T_x(E), \qquad T_y(E)$$

by direct resolvent calculation and, where the reduced-chain approximation applies, by the recurrence and transfer-matrix methods of Section 3.

(C4) Determine optical and redox quantities. Calculate or measure the absorption response, E_{00}, oxidation and reduction potentials, and the free-energy quantities

$$\Delta G_{\mathrm{CS}}, \qquad \Delta G_{H}.$$

Every potential shall be converted to the common reference scale before free energies are combined.

(C5) Estimate kinetic and transport factors. Determine or bound

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

including lifetime, diffusion-length, catalyst-distance, and interfacial-transfer assumptions.

(C6) Perform mass normalization. Calculate the complete primitive-cell molar mass using Section 4. Report the dry and conditioned masses separately whenever metals, counterions, solvent, or residual species are present.

(C7) Propagate joint uncertainty. Construct simultaneous lower bounds using the procedure of Section 5. Preserve covariance arising from common geometries, spectra, kinetic fits, or experimental replicates.

(C8) Apply the prospective decision rule. Calculate

$$t_{\min} = \min\{|T_x(E^*)|, |T_y(E^*)|\}$$

and

$$R^{\mathrm{LB}}_{\mathfrak{R}_N} = \frac{1}{2}\underline{\mathcal{A}}_N \underline{\Phi}_{\mathrm{CS},N}\underline{\Phi}_{\mathrm{tr},N}\underline{\Phi}_{\mathrm{inj},N}\underline{\eta}_{\mathrm{Pt},N}.$$

A candidate advances to prospective measurement only if all predeclared structural, energetic, kinetic, and detectability inequalities are satisfied.

(C9) Lock predictions before experimental unblinding. Archive the predicted structure, properties, intervals, thresholds, and decision outcome before optical, electrochemical, or hydrogen-evolution measurements are released for that candidate.

(C10) Execute and report the controlled test. Compare the illuminated candidate against dark, no-material, and no-Pt controls. Report positive and negative results under the same prospectively declared analytical procedure.

7.2 Numerical verification requirements

The following internal checks shall be completed before a candidate decision is accepted:

$$\begin{aligned} H_B^{(m)} &= \left(H_B^{(m)}\right)^{\dagger}, \\ D_r(E) &= (E-\varepsilon_r)D_{r-1}(E) - |\tau_{r-1}|^2 D_{r-2}(E), \\ T_m^{\mathrm{direct}}(E) &\simeq T_m^{\mathrm{recurrence}}(E), \\ \mathcal{M}_{\mathrm{cell}}^{\mathrm{res}} &\simeq \mathcal{M}_{\mathrm{cell}}^{\mathrm{pre}} - \mathcal{M}_{\mathrm{loss}}, \end{aligned}$$

within prospectively specified numerical tolerances. Monte Carlo or bootstrap bounds shall be checked for convergence with respect to the number of draws, and results near a resolvent pole shall be repeated with the declared broadening and full block Hamiltonian.

Definition 20 (Prospective decision record)**.** *The decision record is*

$$\mathscr{D}_N^{(q)} = \left(E^*, t_{\mathrm{crit}}, \delta_{\mathrm{CS}}, \delta_H, \phi_{\mathrm{CS,min}}, R_{\mathrm{LOQ}}, \alpha, R^{\mathrm{LB}}_{\mathfrak{R}_N}, \mathrm{Decision}\right),$$

where

$$\mathrm{Decision} \in \{\mathsf{Advance}, \mathsf{Reject}, \mathsf{Unresolved}\}.$$

A missing lower bound, failed calibration, unconverged calculation, or unspecified provenance produces the decision Unresolved*, not* Advance*.*

7.3 Software, data, and archival record

Every executable calculation shall record:

1. software name, version, and relevant source-code revision;
2. functional, basis set, pseudopotential, dispersion correction, solvation model, and convergence criteria;
3. operating environment and hardware information when numerically consequential;
4. random seeds for stochastic fitting, sampling, or model training;
5. dataset version, split identifiers, and preprocessing rules;
6. input- and output-file checksums; and
7. date, operator, and candidate identifier.

Publicly releasable structures, scripts, and derived data shall be archived with the article or in a persistent repository. Where proprietary molecular inputs cannot be disclosed, their immutable checksums, calculation settings, and nonconfidential derived results shall be retained in an auditable record. No proprietary result is treated as independently reproducible merely because its existence is asserted.

Remark 11 (Reproducibility standard)**.** *The reproducibility bundle establishes what was calculated, under which assumptions, and before which experimental observations. It does not convert a computational prediction into an experimental result. Reproducibility, prospective locking, and controlled measurement are separate requirements for Phase I feasibility.*

Conclusion

This Supplemental Information converts the main article's conditional feasibility statement into a reproducible calculation sequence for 3, 6, 9, 12-connected rectangular chrysene networks. The resulting framework does not infer photocatalytic activity from visible absorption, geometric density, or structural similarity to the DBC benchmark. Instead, it requires separate support for electronic coupling, energetic alignment, charge separation, carrier survival, catalyst access, interfacial injection, and analytical detectability.

The bridge recurrence shows how the unequal N- and $N+2$-order directions may be compared without assuming isotropy. Within the homogeneous reduction,

$$\eta_T(E;N) = \frac{|T_y(E;N)|}{|T_x(E;N)|} = \chi_\gamma(E;N)\left|\frac{U_{\ell_0+N}(z(E))}{U_{\ell_0+N+2}(z(E))}\right|.$$

The longer bridge generally incurs an electronic-coupling penalty, but finite bridge extension does not by itself force

$$T_y(E;N) = 0.$$

Admissible bridge orders are those satisfying

$$N \in \mathcal{N}_{\mathrm{adm}}(E^*) \quad \Longleftrightarrow \quad \min\left\{|T_x(E^*;N)|,\ |T_y(E^*;N)|\right\} \geq t_{\mathrm{crit}}.$$

Primitive-cell accounting establishes that geometric compactness and density per unit mass are different design properties. The translation lengths cancel from the node count per gram:

$$n_V^{(m)}(N) = \frac{N_{\mathrm{A}}}{\mathcal{M}_{\mathrm{cell}}(N)}.$$

Consequently, improvements in areal density cannot be reported as mass-normalized advantages unless primitive-cell composition or per-node photophysical performance also changes. Metal ions, counterions, retained solvent, and longer bridges must all be included in the reported cell mass.

The uncertainty analysis shows that the rate lower bound is certified only on a simultaneous event. If

$$\mathbb{P}\left[X_{i,N} \geq \underline{X}_{i,N} \text{ for all } i\right] \geq 1-\alpha,$$

then

$$R_{\mathfrak{R}_N} \geq \frac{1}{2}\prod_{i=1}^{5}\underline{X}_{i,N}$$

with coverage at least $1-\alpha$. Marginal intervals, point estimates, or independently sampled factors do not provide the same guarantee when common geometries, spectra, or kinetic fits induce covariance. The robust detectability decision is therefore

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

rather than comparison of a best-fit rate with a fixed nominal threshold.

Metal conditioning is represented by

$$\Sigma_M(E;\mathfrak{m}) = V_M(\mathfrak{m})^\dagger\left[EI - H_M(\mathfrak{m})\right]^{-1}V_M(\mathfrak{m}).$$

This construction permits metal-induced shifts, coupling changes, and broadening to be evaluated within a common formalism. It also makes explicit that favorable energetic alignment can be offset by excited-state quenching. A productive metal-mediated separation pathway improves the reduced charge-separation yield only when

$$k_{s,M}k_\ell \geq k_s k_{q,M}.$$

Thus, neither Mg nor a redox-active transition metal is assumed beneficial before its complete conditioned rate bound is evaluated.

The final output for each candidate is a locked reproducibility bundle containing its chemical identity, geometry, Hamiltonians, property predictions, uncertainty construction, thresholds, and advance-or-reject decision. Candidates advance to measurement only after these records are archived. Experimental confirmation then requires a background-corrected lower confidence bound above the assay limit of quantification and prospectively specified comparisons with dark, no-material, and no-Pt controls.

Accordingly, the supplement provides a procedure for deciding whether a rectangular chrysene candidate merits experimental testing and whether the result supports the predicted feasibility conditions. A positive result would establish controlled Pt-assisted hydrogen evolution for the tested material and boundary conditions. A negative result would identify the failed structural, electronic, thermodynamic, kinetic, or analytical inequality. Neither outcome establishes catalyst-free hydrogen production or overall water splitting, but both provide falsifiable information for the subsequent development of chrysene-based artificial-photosynthesis materials.

A Methodological Literature Context

This appendix places the mathematical methods used in the Supplemental Information within the relevant literature. Its purpose is not to infer experimental hydrogen evolution from precedent alone. Rather, it identifies the established theoretical results supporting the bridge-reduction, anisotropic-transport, uncertainty-propagation, and metal-perturbation calculations developed in Sections S1–S6.

A.1 Projection methods and bridge-mediated electronic coupling

The elimination of internal bridge degrees of freedom is an application of partitioning theory. Löwdin partitioning decomposes a Hilbert space into a retained subspace and an eliminated subspace and replaces the latter by an energy-dependent effective operator acting on the former [Löw51]. If

$$\mathcal{H} = \mathcal{H}_P \oplus \mathcal{H}_Q$$

and the Hamiltonian has block form

$$H = \begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix},$$

then elimination of the Q-subspace yields

$$H_{\mathrm{eff}}(E) = H_{PP} + H_{PQ}(EI_Q - H_{QQ})^{-1}H_{QP}.$$

The bridge self-energy and effective node-to-node coupling used in the present work are finite-dimensional instances of this construction.

McConnell's treatment of intramolecular charge transfer established an early superexchange description in which electronic communication between terminal states is mediated by intervening molecular orbitals [McC61]. In an off-resonant bridge, the resulting coupling commonly decreases approximately exponentially with bridge length,

$$|T(N;E)| \sim T_0(E)e^{-\beta(E)N},$$

although the attenuation constant depends on the bridge spectrum, attachment geometry, and energy E. The recurrence developed in Section S2 therefore does not assume a universal value of β; it derives the length dependence from the specified reduced bridge Hamiltonian.

Green's-function formulations relate transmission amplitudes to resolvent matrix elements [FL81]. Recursive and transfer-matrix algorithms provide efficient evaluations of bulk, surface, and finite-chain Green's functions without repeated inversion of the full Hamiltonian [LSLSR85]. These precedents justify computing

$$T_\alpha(E) = \mathbf{v}_{L,\alpha}^{\dagger}(EI - H_{B,\alpha})^{-1}\mathbf{v}_{R,\alpha}, \qquad \alpha \in \{x, y\},$$

by recurrence or transfer matrices.

The present use of this expression is deliberately narrower than a complete quantum-transport calculation. A nonzero value of $T_\alpha(E)$ establishes electronic communication within the reduced model; it does not, by itself, determine macroscopic conductivity, carrier mobility, or a hydrogen-evolution rate.

A.2 Periodic conjugated frameworks and anisotropic transport

The electronic structure of a two-dimensional conjugated framework depends jointly on the frontier states of its nodes, the electronic character of its linkers, the attachment-site coefficients, lattice topology, and interlayer interactions [TLZ+19]. It is therefore generally insufficient to characterize a framework solely through the optical spectrum of an isolated chromophore.

For the rectangular lattice, the two bridge directions need not have equal length or equal effective coupling. The nearest-neighbor Bloch dispersion

$$\varepsilon(\mathbf{k}) = \varepsilon_0 + 2T_x\cos(k_x a_x) + 2T_y\cos\bigl(k_y a_y\bigr)$$

accordingly retains T_x and T_y as independent parameters. This form captures the minimal distinction between a square approximation and the chemically realizable rectangular network. The condition

$$T_x T_y \neq 0$$

is a model-level criterion for two-dimensional spectral dispersion, whereas

$$T_x T_y = 0$$

reduces the nearest-neighbor model to one-dimensional electronic propagation.

The calculation does not equate band dispersion with useful photocatalytic transport. Disorder, exciton binding, dielectric screening, finite domain size, interlayer offsets, and electron–phonon coupling can substantially alter carrier motion in an experimental framework. The periodic Hamiltonian should therefore be interpreted as a falsifiable electronic baseline rather than a quantitative mobility model.

Excited-state energies and optical transitions may be refined through time-dependent density-functional theory. The formal basis for time-dependent density-functional theory was established by the Runge–Gross theorem [RG84]. Practical results nevertheless depend on the exchange–correlation approximation, basis or pseudopotential, dielectric environment, conformational model, and treatment of charge-transfer states. Consequently, the calculation protocol must report these choices and must not combine computed excitation energies with experimental spectra as though they were measurements of the same random variable.

A.3 Uncertainty propagation and sensitivity analysis

The hydrogen-support lower bound in Section S4 is a product of uncertain factors. Guidance for reporting and propagating measurement uncertainty is provided by the Guide to the Expression of Uncertainty in Measurement [Joi08]. For

$$R_{\mathrm{LB}} = R_{\mathrm{abs}}\eta_{\mathrm{CS}}\eta_{\mathrm{tr}}\eta_{\mathrm{Pt}}\eta_{\mathrm{HER}},$$

the logarithmic representation

$$\log R_{\mathrm{LB}} = \log R_{\mathrm{abs}} + \log \eta_{\mathrm{CS}} + \log \eta_{\mathrm{tr}} + \log \eta_{\mathrm{Pt}} + \log \eta_{\mathrm{HER}}$$

makes multiplicative sensitivity explicit and prevents a single poorly constrained factor from being hidden by aggregation.

First-order uncertainty propagation is appropriate only when the map is locally smooth and the uncertainties are sufficiently small. Bootstrap resampling provides a less restrictive method for estimating sampling variability and confidence intervals from finite datasets [Efr79]. Global variance-based indices, including Sobol indices, are appropriate when nonlinearities and interactions make local derivatives inadequate [Sob01]. These methods are complementary: logarithmic elasticities identify local multiplicative sensitivity, whereas Sobol indices apportion output variance over a prescribed joint input distribution.

When a machine-learning predictor supplies optical or redox inputs, calibration must be assessed separately from point error. Conformalized quantile regression provides a distribution-free route to marginal prediction-interval coverage under exchangeability assumptions [RPC19]. Such coverage is not automatically simultaneous over all factors in R_{LB}, nor does it remain guaranteed under uncontrolled domain shift. The Supplemental Information therefore distinguishes model uncertainty, parameter uncertainty, measurement uncertainty, and structural uncertainty.

A.4 Metal-ion conditioning and catalytic interfaces

Metal incorporation can modify orbital energies, excited-state lifetimes, charge localization, and catalytic accessibility, but metal addition is not intrinsically beneficial. Isostructural metalloporphyrin covalent organic frameworks have shown that changing metal identity can change charge-carrier dynamics and photocatalytic hydrogen evolution even when the surrounding framework is closely related [CWM+21]. This establishes the importance of treating metal identity and coordination as explicit variables. It does not establish that Mg, Fe, or another metal will improve the proposed chrysene network.

The perturbative model in Section S5 writes the metal-conditioned node Hamiltonian as

$$H_{\mathrm{node}}^{(M)}(E) = H_{\mathrm{node}}^{(0)} + V_{NM}(EI - H_M)^{-1}V_{MN}.$$

This Schur-complement form separates the unconditioned network from the metal-state subspace. It also makes the breakdown of perturbation theory explicit: if E approaches the spectrum of H_M, or if $\|V_{NM}\|$ is not small relative to the relevant level separation, a full coupled-state treatment is required.

Electron-transfer kinetics depend on electronic coupling, reaction free energy, nuclear reorganization, and temperature, as formalized in Marcus theory [Mar93]. A metal-induced increase in optical absorption or density of states therefore need not increase productive charge transfer. The same perturbation may introduce trap-assisted recombination, excited-state quenching, or unfavorable redox shifts.

The terminal cocatalyst must likewise be treated independently from the light-absorbing framework. Studies of platinum deposited on covalent organic frameworks show that catalyst placement and interfacial electronic communication can materially affect photocatalytic hydrogen production [LYH+22]. This supports retaining η_{Pt} as a separate factor rather than absorbing it into an intrinsic lattice-coupling parameter.

A.5 Reproducibility and evidentiary status

Reproducibility studies in density-functional theory demonstrate that well-specified calculations can agree across implementations, while also showing that numerical settings, pseudopotentials, basis representations, and convergence criteria must be documented [L+16]. The calculation sequence in Section S6 therefore records the molecular geometry, bridge length, electronic-structure method, environmental model, energy reference, matrix construction, convergence thresholds, and software version.

The FAIR principles provide a complementary framework under which numerical inputs, metadata, scripts, and outputs should be findable, accessible, interoperable, and reusable [W+16]. For the present model, a reproducible computational record should minimally contain

$$\mathscr{R} = (\mathcal{G}, \Theta, H_B, H_{\mathrm{node}}, V, \mathcal{D}, \mathcal{A}, O),$$

where $\mathcal{G}$ is the structural graph, Θ is the parameter set, $\mathcal{D}$ is the input dataset, $\mathcal{A}$ is the ordered calculation procedure, and O is the set of reported outputs.

Remark 12 (Limits of the cited precedent)**.** *The literature reviewed above establishes the legitimacy of the mathematical and computational tools used in the Supplemental Information. It does not establish that the proposed 3,6,9,12-connected chrysene network evolves hydrogen. In particular,*

$$\textit{methodological precedent} \not\Longrightarrow R_{\mathrm{H_2}} > 0.$$

The latter proposition remains a prospective experimental hypothesis requiring controlled illuminated, dark, no-material, no-cocatalyst, and benchmark measurements.

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