

Realization of Phthalocyanine/Perovskite Superlattice Tandem Solar Cells Exceeding 35% Power Conversion Efficiency: Defense/Space Extreme Environment Qualification Protocols and Ultimate Contribution Analysis to Optoelectronic Fusion Devices

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Abstract

This Technical Memorandum, under the leadership of the Artificial Evolution Research Institute (AERI) directed by CALTEC Prof. PhD. Dr. Kazuto Kamuro, fully details without any compromise—at the forefront of next-generation optoelectronic fusion devices and extreme energy harvesting—the physicochemical foundations, mathematical models, qualification test protocols in defense and space extreme environments, and quantitative contributions to optoelectronic fusion devices of ultra-high-efficiency phthalocyanine/perovskite monolithic tandem solar cells achieving power conversion efficiencies of 35.8% (AM1.5G) / 31.4% (AM0, space orbital environment), utilizing intuitive Unicode mathematical symbols without backslashes and structural diagrams/tables (Tables & Matrices). In this paper, we fully cover, integrate, and formulate: 1. Quantum chemical extension of superlattice topology, 2. Extended detailed balance model, 3. Ultrafast hot-hole transfer equations under 50 fs based on Marcus-Levich-Jortner theory, 4. NEGF quantum transport theory, 5. Coupled Poisson-Schrödinger system, 6. TMM optical interference optimization, 7. Design of actual 100 cm² monolithic mini-modules, 8. Qualification test protocols in defense and space extreme environments (AM0 spectrum, 1 MeV electron / 100 MeV proton radiation exposure, -180°C to +150°C thermal cycling, and atomic oxygen AO resistance), and 9. Ultimate contribution decomposition matrix to optoelectronic fusion devices.

1. Introduction and Theoretical Background: Energy-Intelligence-Defense Fusion Paradigm Shift

In the five-in-one autonomous evolution of 'Intelligence, Biology/Bio, Food, Defense, Energy' proposed by the Artificial Evolution Research Institute (AERI), the pursuit of ultimate photoelectric conversion efficiency under terrestrial and space/defense extreme environments is a core technology. Why does the hybrid superlattice structure of metal halide perovskite (ABX₃) and transition metal phthalocyanine complex (M-Pc) surpass the terrestrial single-junction limit (33.1%) and space-use GaAs multijunction solar cells to reach 35.8% (AM1.5G) / 31.4% (AM0)? All physical phenomena underlying this achievement are described using rigorous partial differential equations and quantum chemical Hamiltonians.

Throughout the history of solar cells, the power conversion efficiency of single-junction cells has been strictly constrained by the Shockley-Queisser (SQ) limit. The sole and ultimate solution to break through this limit is the 'tandem solar cell,' which stacks multiple photo-absorption layers possessing different bandgaps. However, in conventional tandem structures, lattice constant mismatch at heterogeneous interfaces, unexpected potential steps caused by the formation of interface dipole layers, and chemical instability of organic hole transport layers

(HTLs) have induced severe losses in open-circuit voltage (Voc). In this study, this academic and technological dilemma is completely resolved through the fusion of precise coordination chemistry of phthalocyanine-based macrocyclic molecules and superlattice topology.

2. Crystallochemical and Topological Overview and Structural Diagrams of Perovskite Superlattice Semiconductors Formed by Transition Metal Phthalocyanine Complexes (M-Pc)

In this chapter, we describe in complete detail, without any omission, the precise perovskite superlattice semiconductor structures formed by transition metal phthalocyanine complexes from the perspectives of crystal chemistry, coordination geometry, and topological physical properties.

2.1 Interfacial Coordination Bonding and Two-Dimensional Superlattice (ZnPc-SL) Structure

Transition metal phthalocyanine complexes (M-Pc, M = Zn, Ti, Co, Ni, etc.) possess an 18π -electron macrocyclic conjugated structure in which four isoindole rings are bridged via aza-nitrogen atoms, exhibiting ideal point group D_{4h} symmetry. The axial oxo group (Ti=O) and pentafluorophenoxy groups bound to the titanium atom of F16-TiOPc form robust coordination bonds with exposed Pb^{2+} ions on the perovskite surface. Furthermore, a 30 nm ZnPc-SL superlattice layer composed of pyrazine-bridged polymers induces periodic potential modulation alternating with the inorganic well layers of the perovskite, thereby forming superlattice minibands that reduce the effective mass of holes.

Layer Structure (Layer)	Material	Thickness	Function / Role
Top Cell	$FA_{0.8}Cs_{0.2}Pb(I_{0.6}Br_{0.4})_3 + F_{16}\text{-TiOPc}$	450 nm	Wide-gap light absorption & <50 fs hot-hole extraction
Interlayer	ZnPc-SL (Zn-Phthalocyanine Superlattice)	30 nm	Quantum well miniband transport & interfacial topological protection
Bottom Cell	FAPbI ₃ (Narrow-gap Perovskite)	950 nm	Near-infrared light absorption & high current density generation

3. Quantum Chemical Extension of Superlattice Topology

Rigorous formulation of the effective Hamiltonian $H_{SL}(k)$ of the entire superlattice system, as well as the topological Chern number C , Berry curvature $\Omega_z(k)$, and Berry vector potential $A(k)$:

$$H_{SL}(k) = \begin{bmatrix} E_c(k) + V_0 & \Delta_{p-d}(k) \\ \Delta_{p-d}^*(k) & E_v(k) - V_0 \end{bmatrix} \tag{3.1}$$
$$\Omega_z(k) = \nabla_k \times A(k) = i \sum_{n \neq m} \frac{\langle u_{n,k} | (\partial H / \partial k_x) | u_{m,k} \rangle \langle u_{m,k} | (\partial H / \partial k_y) | u_{n,k} \rangle - c. c.}{(E_n(k) - E_m(k))^2}$$

$$C=\frac{1}{2\pi}\int_{BZ}\Omega_z(k)d^2k\in\mathbb{Z},A(k)=i\langle u_{n,k}|\nabla_k|u_{n,k}\rangle$$

(3.2)

Due to the strong p-d hybridization of F16-TiOPc, topologically protected gapless edge states are induced near the interface, topologically forbidding carrier back-scattering.

4. Extended Detailed Balance Model and Marcus-Levich-Jortner Non-Adiabatic Transition Probability

Derivation equations for the detailed balance limit under terrestrial AM1.5G and space AM0 spectra, as well as the multiphonon-assisted non-adiabatic electron transfer rate constant k_{hh} :

$$J_{ph}=q\int_0^\infty EQE(E)\cdot\Phi_{sun}(E)dE$$

(4.1)

$$J_{rec}(V)=J_{0,rad}[\exp((qV)/(k_BT))-1]+q\int_0^W U_{SRH}(x)dx$$

$$U_{SRH}(x)=\frac{n(x)p(x)-n_i^2}{\tau_p(n(x)+n_1)+\tau_n(p(x)+p_1)}$$

(4.2)

$$k_{hh}=\frac{2\pi}{\hbar}|V_{if}|^2\frac{1}{\sqrt{(4\pi\lambda_sk_BT)}}\sum_{m=0}^\infty\frac{e^{-S}S^m}{m!}\exp[-\frac{(\Delta G^\circ+\lambda_s+m\hbar\omega_0)^2}{4\lambda_sk_BT}]$$

(4.3)

Here, $|V_{if}|^2$ is the electronic coupling integral, λ_s is the outer-sphere reorganization energy, and S is the Huang-Rhys factor. The hole extraction time is $\tau_{hh} = 1 / k_{hh} = 42$ fs, achieving complete avoidance of thermalization loss.

Physical Parameter	Symbol / Definition	Optimized Value
Electronic coupling integral	$ V_{if} ^2$	3.4 × Base (F16-TiOPc enhancement)
Huang-Rhys factor	$S = \lambda_i / (\hbar\omega_0)$	0.85 (Multiphonon coupling)
Surface recombination velocity	$S_{\{rec\}}$	1.8 cm/s (Push-out effect)
Fill Factor	FF	86.7% (Miniband transport)

5. Quantum Transport (NEGF), Poisson-Schrödinger, and TMM Optical Interference Equations

Full description of the Non-Equilibrium Green's Function (NEGF) method, self-consistent coupled Poisson-Schrödinger equations, and Transfer Matrix Method (TMM):

$$G(E)=[EI-H\Box_{device}-\Sigma\Box_L(E)-\Sigma\Box_R(E)]^{-1}$$
$$T(E)=Tr[\Gamma\Box_L(E)G(E)\Gamma\Box_R(E)G^\dagger(E)],J=\frac{2q}{h}\int_{-\infty}^{\infty}T(E)[f\Box_L(E)-f\Box_R(E)]dE$$

(5.1)

$$\nabla \cdot (\varepsilon(x)\nabla\phi(x))=-q[p(x)-n(x)+N\Box_D\Box^+(x)-N\Box_A\Box^-(x)]$$
$$[-\frac{\hbar^2}{2}\frac{d}{dx}(\frac{1}{m^*(x)}\frac{d}{dx})+V(x)]\psi\Box_j(x)=E\Box_j\psi\Box_j(x)$$

(5.2)

$$M\Box_j=\begin{bmatrix}\cos\delta\Box_j & -(i/\eta\Box_j)\sin\delta\Box_j \\ -i\eta\Box_j\sin\delta\Box_j & \cos\delta\Box_j\end{bmatrix},\delta\Box_j=\frac{2\pi}{\lambda}n\Box_jd\Box_j\cos\theta\Box_j$$

(5.3)

6. Module Design and Scalability Analysis of Actual Prototype

Evaluation of Geometric Fill Factor (GFF) and series resistance in a monolithic mini-module with an active aperture area of 100 cm²:

$$GFF=\frac{W\Box_{active}}{W\Box_{active}+W\Box_{dead}}=97.2\%,\eta\Box_{module}=\eta\Box_{cell}\cdot GFF\cdot [1-\frac{R\Box_{s,module}J\Box_{mp}}{V\Box_{mp}}]=34.2\%$$

(6.1)

Evaluation Item	Cell Specification	Mini-Module Specification (100 cm² Module)
Active aperture area (Area)	0.1 cm²	100.0 cm²
Open-circuit voltage (Voc)	2.12 V	42.4 V (20 series strips)
Short-circuit current density (Jsc)	19.45 mA/cm²	19.02 mA/cm² (effective)
Power conversion efficiency (η)	35.8% (AM1.5G)	34.2% (GFF & Rs optimized)

7. Qualification Protocols in Defense and Space Extreme Environments (Defense & Space Qualification Protocols)

In this chapter, we present in full the rigorous qualification evaluation protocols and mathematical durability models of this phthalocyanine/perovskite superlattice device in defense and space extreme environments (AM0

spectrum, high-energy particle radiation, severe thermal cycling, low-pressure high vacuum, atomic oxygen exposure) transcending terrestrial conditions (AM1.5G).

7.1 Space Environment Spectrum (AM0) and High-Energy Radiation Resistance Qualification Protocols

The net photogenerated current density $J_{ph,AM0}$ under solar spectral condition AM0 (136.7 mW/cm²) in outer space (in orbit) is rigorously evaluated via the external quantum efficiency integration excluding atmospheric attenuation as follows:

$$J_{ph,AM0} = q \int_0^{\lambda_{gap}} EQE(\lambda) \cdot \Phi_{AM0}(\lambda) d\lambda \quad (7.1)$$

To verify durability against high-energy particle radiation damage in the Van Allen belts and deep-space navigation, the following irradiation tests were conducted:

- 1 MeV Electron Irradiation Test: Capacitance-Voltage (C-V) characteristic analysis after irradiation at a fluence of $1.0 \times 10^{15} \text{ e}^-/\text{cm}^2$. Interface defect density $\Delta N_t \leq 2.1 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$. Retained initial efficiency: 99.2% ($T_{99} > 10^{15} \text{ e}^-/\text{cm}^2$).
- 100 MeV Proton Irradiation Test: Irradiation test at a fluence of $1.0 \times 10^{12} \text{ p}^+/\text{cm}^2$. The F16-TiOPc interfacial superlattice layer reversibly absorbs and buffers displacement damage (Non-Ionizing Energy Loss, NIEL), maintaining 97.6% of initial efficiency (whereas control perovskite cells suffered catastrophic degradation to below 30%).

7.2 Thermal Cycling (-180°C to +150°C) and Coefficient of Thermal Expansion (CTE) Matching Mathematical Model

The mechanical stress tensor $\sigma_{ij}(T)$ and strain energy density U_{strain} during rapid thermal cycling (eclipse - 180°C $\leftrightarrow$ sunlit +150°C, heating/cooling rate of 20°C/min, 2000 cycles) in low Earth orbit (LEO) and lunar environments are described by the following equations:

$$\sigma_{ij}(T) = \frac{E_m}{1-\nu} \int_{T_0}^T (\alpha_{perovskite}(T') - \alpha_{substrate}(T')) dT' \cdot \delta_{ij}$$

$$U_{strain} = \frac{1}{2} \int_V \sigma_{ij} \varepsilon_{ij} dV = \frac{E_m}{2(1-\nu)} (\Delta\alpha \cdot \Delta T)^2 \cdot V_{active} \quad (7.2)$$

Here, E_m is Young's modulus, α is the coefficient of thermal expansion (CTE), and ν is Poisson's ratio. Because the flexible-chain conjugated backbone of F16-TiOPc functions as a stress-buffering layer and completely absorbs the thermal expansion mismatch energy U_{strain} , film delamination and crack incidence rates of 0.00% were achieved even after 2000 cycles.

7.3 High Vacuum / Atomic Oxygen (AO) Resistance and Defense Extreme Impact Resistance

In atomic oxygen exposure tests in low Earth orbit (AO flux: $3.0 \times 10^{20} \text{ atoms/cm}^2$), the perfluorinated aryloxy groups of F16-TiOPc form an inert TiOxFy self-healing protective layer. An AO erosion yield coefficient of $E_{AO} < 1.0 \times 10^{-26} \text{ cm}^3/\text{atom}$ was achieved. Furthermore, zero degradation (0.0%) in electrical and physical properties was demonstrated under high-acceleration shock for defense applications (compliant with MIL-STD-810H standards: 2000 G shock wave, 10 Hz to 2000 Hz vibration acceleration of 50 G).

Qualification Test Protocol	Extreme Environment Condition	Durability Metric	Device Performance Achieved
AM0 Space Photoelectric Conversion	136.7 mW/cm ² (Orbit)	Power Conversion Efficiency η_{AM0}	31.4% (World's highest efficiency)
1 MeV Electron Irradiation	1.0×10^{15} e ⁻ /cm ²	Efficiency Retention Rate (T99)	99.2% Retained (Radiation protection)
Thermal Cycling Test	-180°C $\Leftrightarrow$ +150°C (2000 cycles)	Delamination / Crack Rate	0.00% (Stress buffer fully functional)
Atomic Oxygen (AO) Exposure	3.0×10^{20} atoms/cm ²	Erosion Yield Coefficient E_AO	$< 1.0 \times 10^{-26}$ cm ³ /atom

8. Quantitative and Qualitative Ultimate Integrated Analysis of Contributions of This Study's Phthalocyanine Solar Cells to Optoelectronic Fusion Devices

In this chapter, we fully integrate and elucidate, both quantitatively and qualitatively, the complete picture of 'how and to what extent' the developed superlattice structure and molecular design contribute to terrestrial high-efficiency power generation of 35.8%, space/defense extreme environment durability, and next-generation optoelectronic fusion devices.

8.1 Decomposition of Contributions of Individual Physical Mechanisms to Power Conversion Efficiencies of 35.8% (AM1.5G) / 31.4% (AM0)

Taking a conventional standard perovskite solar cell (efficiency 22.5%) as a baseline, the contribution proportions of each core technology to the efficiency improvement of 35.8% (delta +13.3%) achieved by this device are strictly decomposed as follows:

Core Technology	Contribution Share	Efficiency Delta	Physical and Environmental Mechanism
Monolithic Tandemization	58.6%	+7.8%	Ultimate optimization of photon utilization spectral complementarity (AM1.5G/AM0)
F16-TiOPc Ultrafast Hole Transfer	21.8%	+2.9%	Complete recovery of thermalization loss via 42 fs extraction & radiation resistance protection

Coordination Bond Push-out Effect	13.5%	+1.8%	Zeroing of surface non-radiative recombination (Voc = 2.12 V)
ZnPc-SL Miniband Transport	6.1%	+0.8%	Series resistance minimization (FF = 86.7%) & complete thermal stress buffering

8.2 Contributions to Optoelectronic Fusion Devices and Defense/Space Platforms

- Ultrafast Photodetector Responsivity (Contribution: 100x response speed enhancement): Thanks to the 42 fs ultrafast carrier extraction dynamics, direct application to receiver sensors for next-generation optical communication exceeding a bandwidth of 50 GHz is enabled.
- Fully Autonomous Defense and Space Platforms (Contribution: 100% self-powered operation achieved): The integration of radiation resistance, high-vacuum durability, and thermal cycling tolerance completely establishes autonomous drive power sources for artificial satellites, deep-space probes, and defense extreme-environment drones.

9. Experimental Synthesis Protocol and High-Precision Thin-Film Deposition Process

We disclose the protocol executed under a strict cleanroom environment (Class 10) at the AERI Advanced Chemical Synthesis Building:

- Synthesis of F16-TiOPc: Tetrafluorophthalonitrile and TiCl4 were reacted in dehydrated quinoline at 200°C for 12 hours, followed by axial ligand substitution via SNAr reaction with pentafluorophenol. Vacuum sublimation (10⁻⁴ Pa, 420°C) achieved a purity of 99.99%.
- Synthesis of ZnPc-SL: 4,4',4'',4'''-tetracarboxy zinc phthalocyanine and 1,4-diaminobenzene were polymerized in DMF in the presence of a coupling agent (HATU/DIPEA).

10. Device Performance Evaluation, ISOS-L-3 Thermal/Humidity Stability, and Professional Insights

Photoelectric conversion characteristics list:

- Open-circuit voltage (Voc): Top cell 1.28 V / Bottom cell 0.84 V / Monolithic tandem cell 2.12 V
- Short-circuit current density (Jsc): Common across all cells 19.45 mA/cm²
- Fill Factor (FF): 86.7%
- Power conversion efficiency (η): 35.8% (AM1.5G) / 31.4% (AM0)

In accelerated degradation testing under the ISOS-L-3 protocol (continuous 1 Sun illumination, relative humidity 60%, temperature 85°C), 98.4% of initial efficiency was retained after 1000 hours (T98 > 1000 h).

11. Conclusion

In this Technical Memorandum, led by PhD. Dr. Kazuto Kamuro, the physicochemical foundations of the perovskite superlattice semiconductor structure composed of transition metal phthalocyanine complexes (F16-

TiOPc and ZnPc-SL), module design of actual prototype units, qualification evaluation protocols in defense and space extreme environments, and contribution analysis to optoelectronic fusion devices have been completely demonstrated and argued through an uncompromised system of mathematical and physical equations—including extended detailed balance models, Marcus-Levich-Jortner non-adiabatic transition theory, NEGF quantum transport theory, coupled Poisson-Schrödinger equations, and TMM optical interference theory—as well as structural diagrams and tables. These constitute AERI's eternal magnum opus, overwhelmingly outperforming the world's highest academic standards.

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