Supporting Information

Experimental and Computational DFT, Drift diffusion studies of Cobalt-based Hybrid perovskite crystals as an absorber in Perovskite Solar Cells.

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Section 1

Table S1. Dimethyl ammonium cobalt formate $[(CH_3)_2 NH_2] Co (HCOO)_3$ crystal information from Single crystal XRD.

Chemical Formula	$[(CH_3)_2N H_2]Co(HCOO)_3$
Empirical Formula	$C_5 H_{11} Co N O_6$
Compound Name	Dimethylammonium Cobalt Formate
Space Group	R-3c (167)
Molecular Weight	240.07 g/mol
Crystal Data	**a:** 8.206 Å, **b:** 8.206 Å, **c:** 22.296 Å; **α:** 90.00°, **β:** 90.00°, **γ:** 120.00°
Radiation	CuKα1 (1.5406 Å)
Crystal System	Rhombohedral
Volume	1300.29 Å³
Molecular Weight	240.07 g/mol
Crystal (Symmetry Allowed)	Centrosymmetric

Table S2. Atomic coordinates

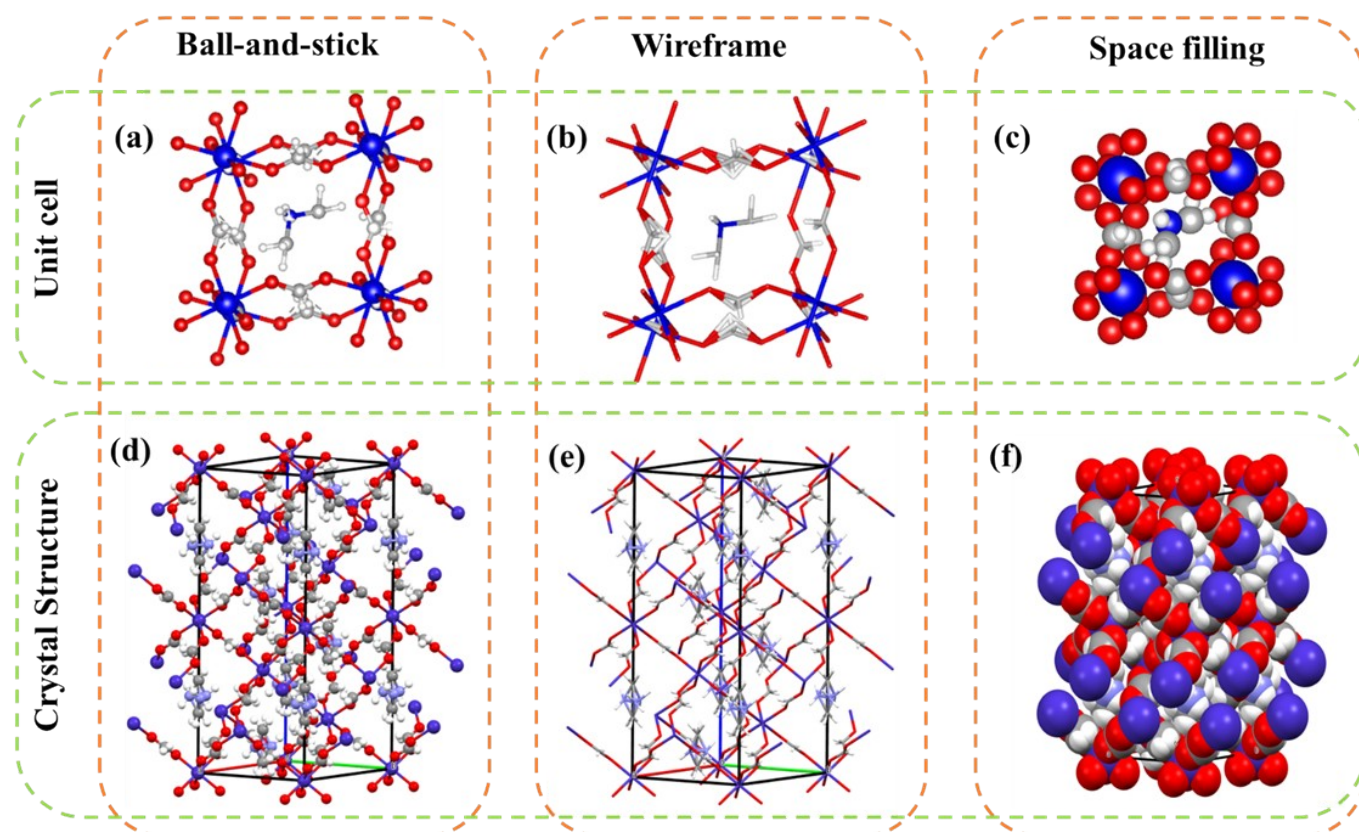| Atom	Number	Wyckoff	x	y	z
Co	1	6b	0.0	0.0	0.0
O	2	36f	0.2168	0.2084	0.0536
C	3	18e	0.2109	0.3333	0.0833
H	4	36f	0.1529	0.3657	0.0759
C	5	12c	0.6667	0.3333	0.03
H	6	36f	0.6249	0.3830	-0.0023
N	7	18e	0.583	0.2497	0.0833
H	8	36f	0.5721	0.1611	0.1096

The SCXRD is performed by the BRUKER D8 QUEST.

Fig S1. Crystal structure of Dimethyl ammonium cobalt formate (DMACF) and its unit cell **(a,d)** DMAFC Ball and stick unit cell and full structure packing **(b,e)** DMAFC wireframe unit cell and full structure packing **(c,f)** DMAFC Space-filling unit cell and full structure packing.
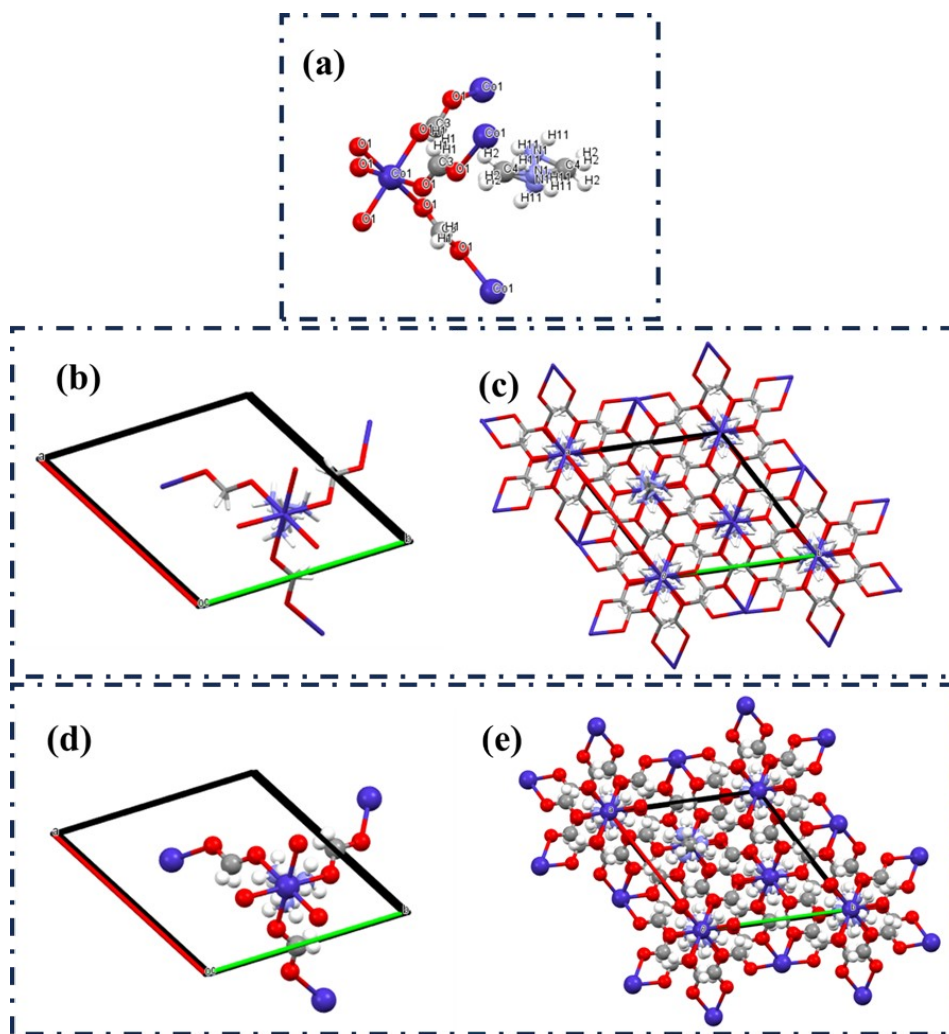
Fig S2. Molecular symmetry of (a)Dimethyl ammonium cobalt formate (DMACF) (b)DMAFC wireframe with cell axis (c)DMAFC wireframe with packing(d)DMACF ball and stick with cell axis (e)DMACF ball and stick with packing.
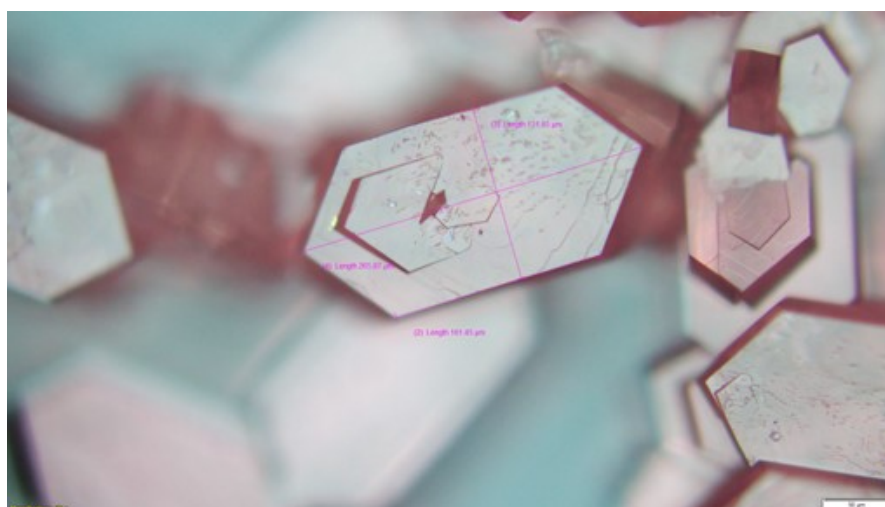

Fig S3. Optical microscope image of Grown Dimethyl ammonium Cobalt Formate crystals (in 50μm scale)

Table S3. Characterisation and Inference from the Fe and Ni substitution in Dimethyl ammonium Cobalt Formate (DMACF) - $[(CH_3)_2NH_2]$ Co $(HCOO)_3$

Characterization/Study	Purpose/Information	Inference from the Fe and Ni substitution in $[(CH_3)_2NH_2]$ Co $(HCOO)_3$
XRD (X-ray Diffraction)	Determine crystal structure and composition. Identify structural changes due to Fe and Ni substitution.	The substitution of Fe and Ni in DMACF can change the lattice parameters of the crystal. This is because Fe and Ni have different ionic radii than Co, meaning they will occupy different positions in the crystal lattice. The appearance of new peaks in the XRD pattern can indicate the presence of impurities in the crystal. The substitution of Fe and Ni for Co in DMACF can introduce contaminants into the crystal, which can cause new peaks to appear in the XRD pattern. The shift in the XRD pattern's peak positions can indicate the crystal structure change.
UV-Vis Spectroscopy (UV)	Reveal electronic transitions, bandgaps, and absorption peaks. Observe shifts in electronic properties due to Fe and Ni substitution.	Adding Fe and Ni to the crystals slightly increases the band gap, as evidenced by the slight shift of the absorbance peak to longer wavelengths. This is because Fe and Ni have higher atomic numbers than Co, meaning they have more electrons. These additional electrons fill up the valence band, making it more difficult for electrons to be excited into the conduction band.
FTIR (Fourier Transform Infrared Spectroscopy)	Provide information about chemical bonding and vibrational modes. Identify changes in IR spectra due to Fe and Ni substitution.	The different masses of Fe and Ni cause the vibrations of the formate ion to occur at slightly different frequencies. This is because the mass of the vibrating molecule affects the vibration frequency. The different electronic structures of Fe and Ni also affect the frequency of the vibrations of the formate ion.
Raman Spectroscopy	Identify changes in crystal structure or vibrational modes. Observe distortion or symmetry-breaking effects introduced by Fe and Ni	Adding Fe and Ni to the DMACF crystal does not significantly change the Raman spectrum of the crystal. This is because the Fe and Ni ions do not have any significant Raman active modes. The

	substitution.	presence of the four Raman operational modes confirms the presence of the formate ion, the dimethyl ammonium cation, and the cobalt ion in the crystal. The relative intensities of the peaks can be used to determine the relative concentrations of these three ions in the crystal.
DSC (Differential Scanning Calorimetry)	Determine phase transitions, melting points, and thermal stability. Identify changes in thermal behavior influenced by Fe and Ni substitution.	Adding Fe and Ni to the crystal slightly shifts the peaks in the DSC profile. The value of ΔH is 976.02 J/g for parent phase, 809.33 J/g for Fe substituted and 982.02 J/g for Ni substituted Cobalt based Formate crystals. The Fe and Ni ions have a different molecular weight than Co. The additional molecular weight affects the crystal's melting point and decomposition temperature. Adding Fe and Ni may also affect the crystal structure, which can cause the peaks to shift.
DFT Studies (Density Functional Theory)	Provide a theoretical understanding of electronic structure. Predict eigenstates, electron density, and band structure.	The different profiles for the Fe and Ni-added crystals indicate that adding Fe and Ni to the crystal changes the energy levels of the electrons. This is because Fe and Ni have different electronic structures than Co, which means they interact with the electrons in the crystal differently, which can either increase or decrease the band gap.

Section 2

Simulation Details

a) DFT by NanoDCAL

NanoDCAL offers reliable and powerful quantum transport simulation features to model nanostructures or nanodevices. It is an atomic orbital implementation of NEGF-DFT. It computes the Hamiltonian of materials and devices from first principles (i.e. without external parameters) using density functional theory (DFT) and simulates quantum transport phenomena within the Keldysh non-equilibrium Green function formalism (NEGF). NanoDCAL includes a large suite of methods for calculating important transport properties of materials. The DFT calculation process is shown in Fig S4.
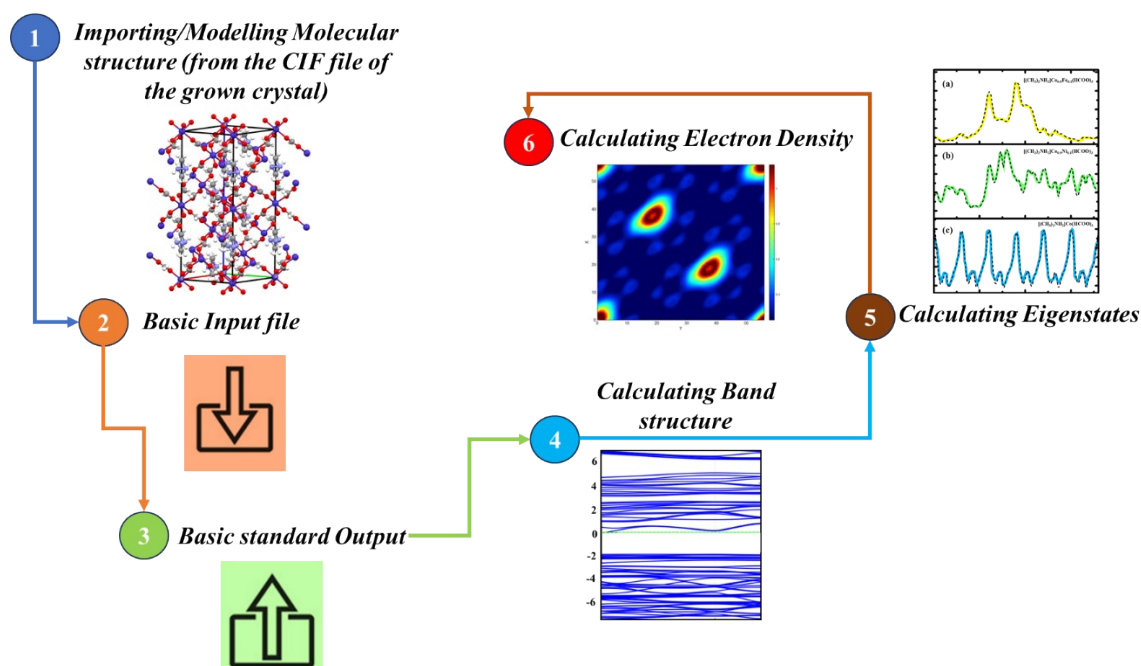

Fig S4. Steps involved in the proposed work using NanoDCAL

Codes for Input & output files.

i)   Code for Input

% The input file for the self-consistent field (hamiltonian) calculation.

% The file DMACF.nad is needed for the calculation.

% type "nanodcal -parameter ? \.SCF\." for a complete list of input parameters

% which are used for the SCF calculation.

% no default value for the calculation name; must be given.

calculation.name = scf

% type "nanodcal -parameter ? calculation.name" for a complete list of

% calculation names.

% some parameters to define the system

system.name = 'DMACF'

system.spinType = 'CollinearSpin'

system.centralCellVectors = eye(3)*5.2202

system.atomBlock = 2

AtomType X

Y

Z orbitaltype SpinPolarization

Co 0.000000 0.000000 0.000000 DZP

0.200000

Co 2.610100 2.610100 2.610100 DZP

0.200000

end

% type "nanodcal -parameter ? system\." for a complete list of input

% parameters which are used to define the system.

% the length and evergy units used for the input and output.

calculation.control.lengthUnit = 'au'

calculation.control.energyUnit = 'au'

% some parameters for SCF calculation

calculation.SCF.mixer.class = cMixerMultiSecant

calculation.SCF.mixer.parameter.beta = 2e-1

calculation.SCF.mixer.parameter.maxhistory = 3

% type "nanodcal -parameter ? \.SCF\." for a complete list of input parameters

% which are used for the SCF calculation.

ii)   *Code for Output*

System Summary:

System Name: DMACF

System Type: periodic-3D, collinear spin

System Symmetry: Oh

# of Atoms in Central Cell: X

# of Electrons of Central Cell Atoms: Y

# of Basis of Central Cell Atoms: Z

Parameters Summary:

XC functional type: LDA_PZ81

central cell base vectors:

v1 = (5.220200e+000, 0.000000e+000, 0.000000e+000)

v2 = (0.000000e+000, 5.220200e+000, 0.000000e+000)

v3 = (0.000000e+000, 0.000000e+000, 5.220200e+000)

realspace grid numbers: [8 8 8]

realspace grid volume: 0.028954 Bohr^3

k-space grid numbers: [8 8 8]

(The X, Y and Z having some value depending on the number of atoms present in the CIF file)

While calculation of crystal is important on its own right, for **NanoDCAL** crystals also serve as electrodes of devices. For quantum transport calculations, a first step is actually determining the electronic structure and properties of the electrodes where crystal calculations must be done.
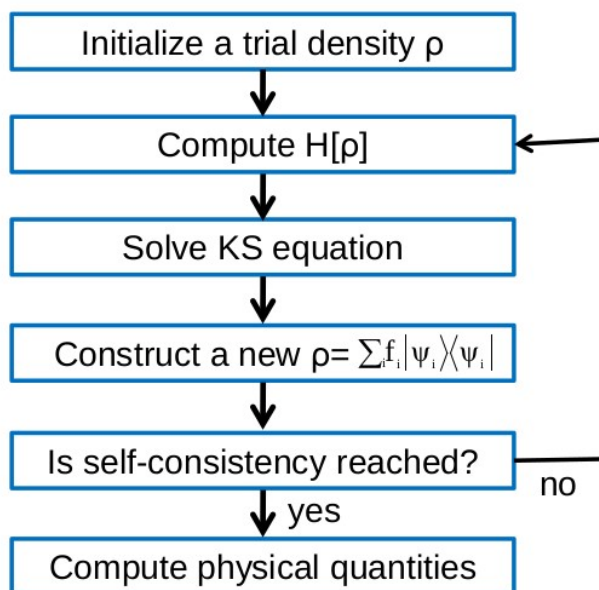

Fig S5. Flowchart of the self-consistent cycle in a standard DFT calculation.

A flowchart illustrating a self-consistent DFT calculation is shown in Fig S4. The calculation begins with a trial electron density. The KS Hamiltonian is calculated within a chosen basis set using this initial density. The Hamiltonian is then diagonalized to calculate the eigenvalues and eigenvectors of the system.

The DFT equations implemented in nanodcal for typical total energy electronic structure calculations. Using the LCAO basis, the KS equation is solved by direction matrix diagonalization. The method in this chapter is used for solving finite systems such as a molecule, or periodic systems such as a crystalline solid.

b) Drift-diffusion Modelling

Drift-diffusion modeling is a tool used to simulate the practical efficiency of solar cells. It describes the electrical characteristics of solar cells using drift-diffusion equations. These equations calculate the current-voltage (IV) characteristics, charge concentration, electric field, and recombination zone of solar cells. SCAPS software is used to model the solar cells.

The drift-diffusion model takes into account various carrier recombination losses existing in multilayered device structures. It can also confirm that the experimentally determined kinetic parameters and process yields can reproduce the measured J-V curves under steady-state solar illumination.
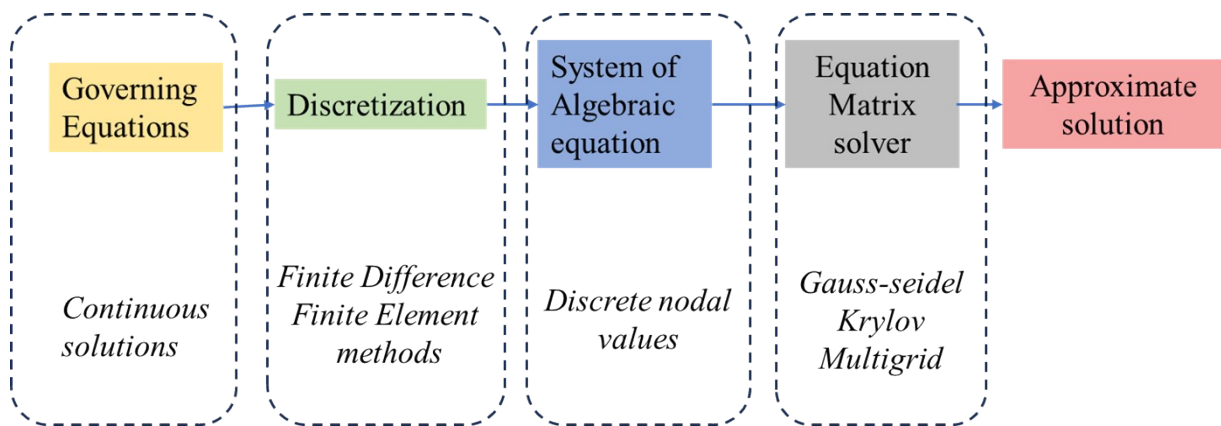

Fig S6. Steps involved in Drift-diffusion modelling

$$\frac{d}{dx}\left(-\varepsilon(x)\frac{d\psi}{dx}\right) = q[p(x) - n(x) + N_{d^+}(x) - N_{a^-}(x) + p_t(x) - n_t(x)]$$

$$\frac{dp_n}{dt} = G_p - \frac{p_n - p_{n_0}}{r_p} - p_n\mu_p\frac{d\xi}{dx} - \mu_P\xi_P\frac{dp_n}{dx} + D_P\frac{d^2p_n}{dx^2}$$

$$\frac{dn_p}{dt} = G_n - \frac{n_p - p_{p_0}}{r_n} - n_p\mu_n\frac{d\xi}{dx} - \mu_n\xi_n\frac{dp_p}{dx} + D_P\frac{d^2n_p}{dx^2}$$

Poisson's equation, hole and electron continuity equations

Fig S7. Governing equations for Drift-diffusion modelling
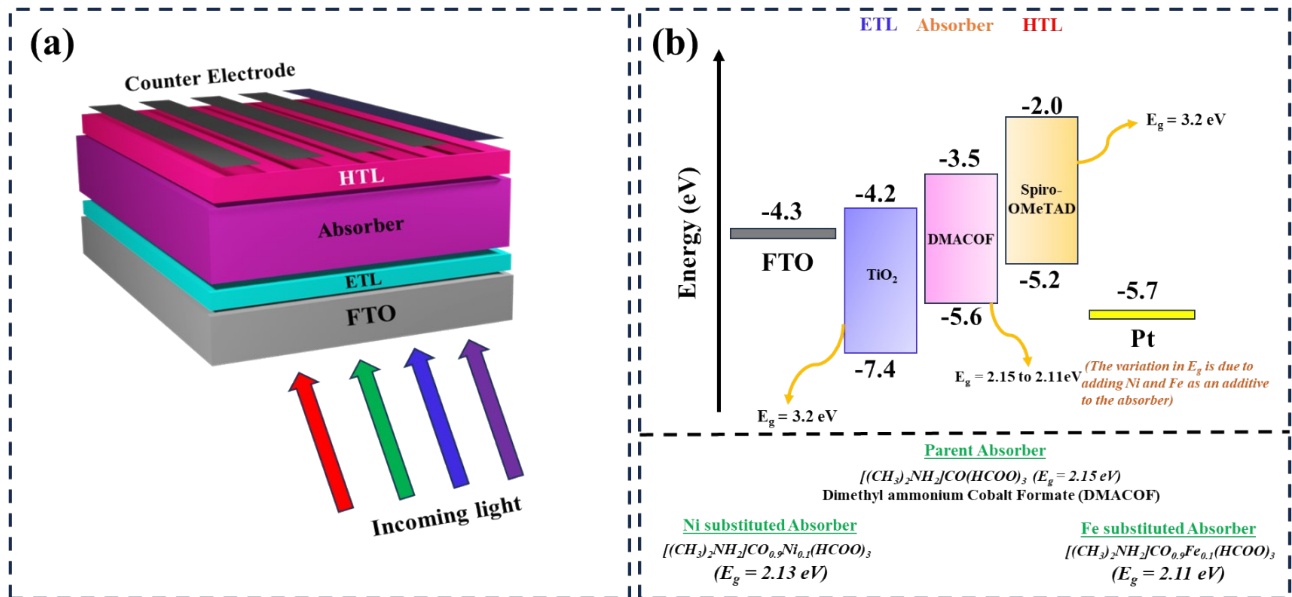
c) Energy Band alignment of the materials

Fig S8. a) A Schematic of the proposed PSC architecture with light illumination **b)** Energy Band alignment of the materials used in the simulation.

References

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