

Supplementary Information

Electron Delocalization in Single-Layer Phthalocyanine-Based Covalent Organic Frameworks: A First Principle Study

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Section S1: The optimized basis set for Mo

Original basis set was taken from the reference:

http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets/Mo_basis.txt

MOLYBDENUM BASIS SETS FOR THE CRYSTAL PROGRAM

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TCM CRYSTAL basis set library: <http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html>

Title: Molybdenum Mo/Mo2+ all-electron

Author: M.D. Towler

When: May 1995

Use: Never used - optimization in atom only

Comment: Remove outer diffuse Gaussian(s) and reoptimize valence functions
for crystals

Results:

	TOTAL HF ENERGY	KINETIC ENERGY	VIRIAL THEOREM
Mo atom (5D)	-3975.3933041	3975.0492866	-2.0000865442
(Roetti/Clementi)	-3975.4280		-2.0000422
difference	+0.0346 Hartree		

Mo2+ ion	-3974.717659	-2.0000544997
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NB: Atomic energies refer to 5s2,4d4 configuration

NB: Mo2+ basis is same as atom with last three free Gaussian functions removed

NB: In semi-ionic situations it is possibly better to remove only the
last two Gaussians from the atomic basis, leaving the shell with
exponent 0.1424.

Mo atom

=====

THIS BASIS SET HAS BEEN DEVELOPED FOR THE FREE ATOM CASE AND SHOULD BE
CONSIDERED A *STARTING POINT* FOR SOLID-STATE CALCULATIONS. REMOVE
ANY DIFFUSE FUNCTIONS (EXPONENTS LESS THAN AROUND 0.1) AND REOPTIMIZE THE
REMAINING EXPONENTS/CONTRACTION COEFFICIENTS OF THE VALENCE FUNCTIONS IN
THE SITUATION OF INTEREST USING e.g. BILLY or LOPTCG. PLEASE SUMMARIZE
RESULTS TO mdt26 at phy.cam.ac.uk

42 11

0 0 9 2.0 1.0

2803592.825747 0.00005

444817.867538 0.000355

97623.996506 0.00215

24043.681147 0.0112

6747.518431 0.0473

2131.383958 0.1567

752.716925 0.3532

293.984852 4244

120.908020 0.1667
0 1 7 8.0 1.0
8300.696289 -0.000336 0.001
1904.293335 -0.00655 0.00936
572.519470 -0.0576 0.0567
198.596466 -0.1475 0.2205
77.368034 0.2011 0.4589
33.814167 0.6759 0.4095
15.491380 0.3038 0.1253
0 1 6 8.0 1.0
180.935425 0.00529 -0.0139
66.122765 -0.0394 -0.0723
27.487516 -0.3338 0.0737
11.638353 0.1347 0.9517
5.152159 0.9806 1.2527
2.264732 0.2897 0.3209
0 3 6 10.0 1.0
293.95 0.00793
87.2824 0.0589
32.1457 0.218
12.9741 0.4242
5.3868 0.4127
2.211 0.1305
0 1 3 8.0 1.0
4.4173 -2.8714 -0.0766
1.9173 0.2991 0.52
0.8516 7.9229 1.0991
0 1 1 0.0 1.0
0.3534 1.0 1.0
0 3 3 4.0 1.0
3.0946 0.1237
1.1746 0.4234
0.4578 0.5112
0 3 1 0.0 1.0
0.1781 1.0
0 1 1 2.0 1.0
0.1424 1.0 1.0
0 1 1 0.0 1.0
0.0623 1.0 1.0
0 1 1 0.0 1.0
0.027 1.0 1.0

Our optimized basis set:

42 10
0 0 9 2.0 1.0
2803592.825747 0.00005

444817.867538 0.000355
97623.996506 0.00215
24043.681147 0.0112
6747.518431 0.0473
2131.383958 0.1567
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0.4578 0.5112
0 3 1 0.0 1.0
0.1781 1.0
0 0 1 2.0 1.0
0.1098 1.0
0 2 1 0.0 1.0
0.1424 1.0

Section S2: Fitting parameters for the deformation potential calculation

In our calculation, the relaxation-time τ is assumed to be primarily by the acoustic phonon. The in-plane stiffness is calculated by fitting the total energy per unit cell to a quadratic function of the longitudinal strain:

$$\Delta E = E - E_o = \frac{1}{2} S_o C_{2D} \times \left(\frac{\Delta l}{l_o}\right)^2 \quad \text{for 2D systems}$$

$$\Delta E = E - E_o = \frac{1}{2} l_o C_{1D} \times \left(\frac{\Delta l}{l_o}\right)^2 \quad \text{for 1D systems}$$

where S_o and l_o are the area and the length of the optimized structures for 2D and 1D systems, respectively. The 2D and 1D stiffness are then calculated from the coefficient of the quadratic fitting curves:

$$C_{2D} = 2 \times \text{coefficient}/S_o \quad \text{for 2D systems}$$

$$C_{1D} = 2 \times \text{coefficient}/l_o \quad \text{for 1D systems}$$

The unit for C^{2D} and C^{1D} are J/m^2 and J/m , respectively.

The DP constant E_1 is calculated in a similar manner. Here, the band edge (VBM or CBM) is also a function of the longitudinal strain:

$$E^{VBM} = E_o^{VBM} + E_1 \times \frac{\Delta l}{l_o} \quad \text{for hole conduction}$$

$$E^{CBM} = E_o^{CBM} + E_1 \times \frac{\Delta l}{l_o} \quad \text{for electron conduction}$$

The effective mass for hole (or electron) is calculated by fitting the valance band (or conduction band) energy to a parabolic function:

$$\varepsilon(\vec{k}) = \varepsilon_o + \frac{\hbar^2}{2m^*} k^2$$

It should be noted that effective mass is a tensor and its value will depend on the direction of fitting. To calculate the intrinsic carrier mobility under DP scheme, the fitting of band energy should be performed in the direction of the strain. Moreover, in our procedure we limit the strain $\Delta l/l_o$ in the range of 5% for stiffness and 1% for DP constant calculation. For effective mass, the wavevector k is limited in the range of 0.05 Bohr^{-1} around the extrema of the bands. These fitting thresholds produce reasonable results and allow one to avoid the uncertainty of DP scheme.¹ More details about theoretical prediction on carrier mobility of organic-nano materials can be found in the previous literature.²⁻⁴

Section S3: Calculated Geometric Parameters

Table S1. Lattice constants and fractional coordinates of the irreducible atoms (Space group P4/mmm, No. 123) for the single-layer NiPc-P, NiPc-2P, and NiPc-3P.

NiPc-P a = 10.591 Å			NiPc-2P a = 13.040 Å			NiPc-3P a = 15.482 Å		
	x	y		x	y		x	y
C	0.60480	0.75876	C	0.09401	0.60891	H	0.00000	0.66015
C	0.88972	0.56637	C	0.58534	0.71041	H	0.15892	0.66196
C	0.00000	0.63627	C	0.81685	0.55412	C	0.00000	0.59004
H	0.00000	0.73838	C	0.00000	0.55549	C	0.07867	0.54674
N	0.72431	0.72431	H	0.09472	0.69197	C	0.15830	0.59198
N	0.50000	0.68157	N	0.68231	0.68231	C	0.57196	0.67733
Ni	0.50000	0.50000	N	0.50000	0.64791	C	0.76704	0.54582
			Ni	0.50000	0.50000	N	0.65362	0.65362
						N	0.50000	0.62476
						Ni	0.50000	0.00000

Table S2. Lattice constants and fractional coordinates of the irreducible atoms (Space group P6/mmm, No. 191) for the single-layer Boroxine-COF, Boronate-COF, Triazine-COF, and CS-COF

Boroxine a = 15.067 Å			Boronate a = 21.606 Å			Triazine a = 14.498 Å		
	x	y		x	y		x	y
H	-0.40519	-0.31101	H	-0.43366	-0.36810	H	-0.40223	-0.30368
C	0.44694	0.05286	O	-0.34718	0.19954	C	0.44457	0.05483
B	0.22602	-0.38699	C	0.46288	0.03685	C	0.22865	-0.38568
O	-0.28087	0.28087	C	-0.33296	0.26953	N	-0.27901	0.27901
C	-0.10778	0.44611	B	0.15669	-0.42165	C	-0.11108	0.44446
			C	-0.07496	0.46252			

CS-COF a = 16.511 Å		
	x	y
H	-0.34865	-0.34865
C	-0.41411	-0.41411
N	-0.33184	0.16634
C	0.49844	0.08386
C	-0.33399	0.24450

Section S4: Thermodynamic Quantities

For entropy calculation in CRYSTAL09, only vibrational degree of freedom is considered in partition function since unlike molecules solid systems are not allowed to rotate and translate. The vibration contributions were taken from the phonon calculations.

Table S3. Thermodynamic quantities at 1 atm at different temperatures for formation reactions

Temp		ΔS (cal/mol.K)	ΔH (kcal/mol)	ΔG (kcal/mol)
350	NiPc-P	-180	-303	-240
	NiPc-2P	-186	-288	-223
	NiPc-3P	-193	-281	-213
450	NiPc-P	-183	-304	-222
	NiPc-2P	-189	-289	-204
	NiPc-3P	-196	-282	-194
500	NiPc-P	-184	-305	-213
	NiPc-2P	-190	-289	-194
	NiPc-3P	-197	-282	-184

Section S6: Intrinsic Charge Mobility for MoS₂

We apply the same approach as reported in the Cai and coworker's paper⁴ to single-layer trigonal prismatic MoS₂. Our calculated band structure from a local Gaussian basis agrees well with their plane wave calculation. It should be noted that the band dispersions are identical irrespective of the exchange-correlation functional used (PBE or B3LYP) even though the band gap are functional dependent. The indirect and direct bandgap by PBE are 1.61 eV (between Γ and M) and 1.73 eV (at K point), respectively. These are in an excellent agreement with the value calculated by the plane wave calculation. The indirect and direct bandgap by B3LYP are 2.26 and 2.44 eV. The previous study shows that bandgap should be direct at K point, while we predict an indirect bandgap at Γ and M point. However, this discrepancy is negligible (0.1 eV) and can be attributed to the perturbation in the lattice constants observed in the previous literature.⁵ To ensure the consistency, we consider the mobility calculation around the K point. Since mobility of MoS₂ are isotropic with respect to the lattice vectors, only a strain along the a direction is calculated for the sake of comparison. From Table S4, the intrinsic charge carrier mobility for hole and electron are 421.74 and 116.94 cm²/V.s, respectively. These are approximately two times higher than the value of 200.52 and 72.16 cm²/V.s from Cai and coworker. Our calculation, however, are consistent with experimental measurement, which provides the optimal mobility in range of 200-500 cm²/Vs for the bulk MoS₂.⁶

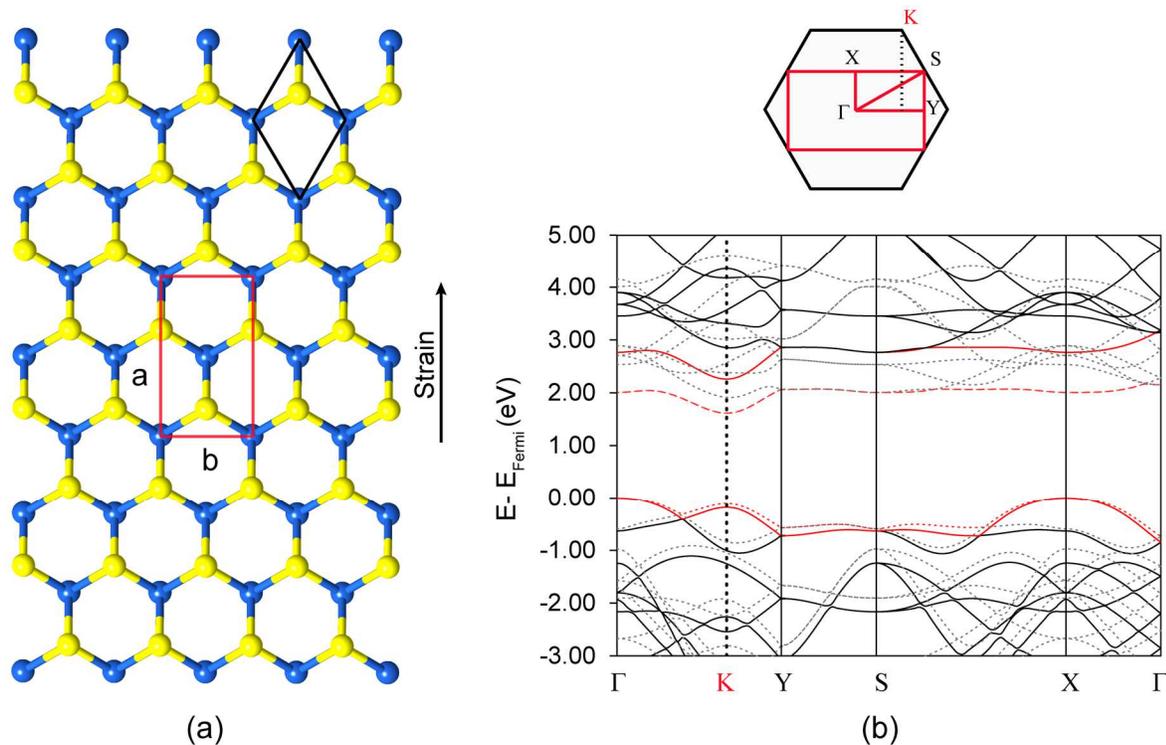


Figure S4. Single-layer structure of MoS₂ (a) and its electronic band structure (b) in the orthorhombic lattice. The top right panel depicts the mapping of K point in the hexagonal lattice onto its coordinate along Γ -Y in the orthorhombic lattice. The electronic band structure of MoS₂ sheet was calculated at the B3LYP (solid curves) and PBE (dashed curves) level of theory. The red curves are the band edges, i.e. VBM (lower) and CBM (upper). Atom colors: Mo, blue; S, yellow.

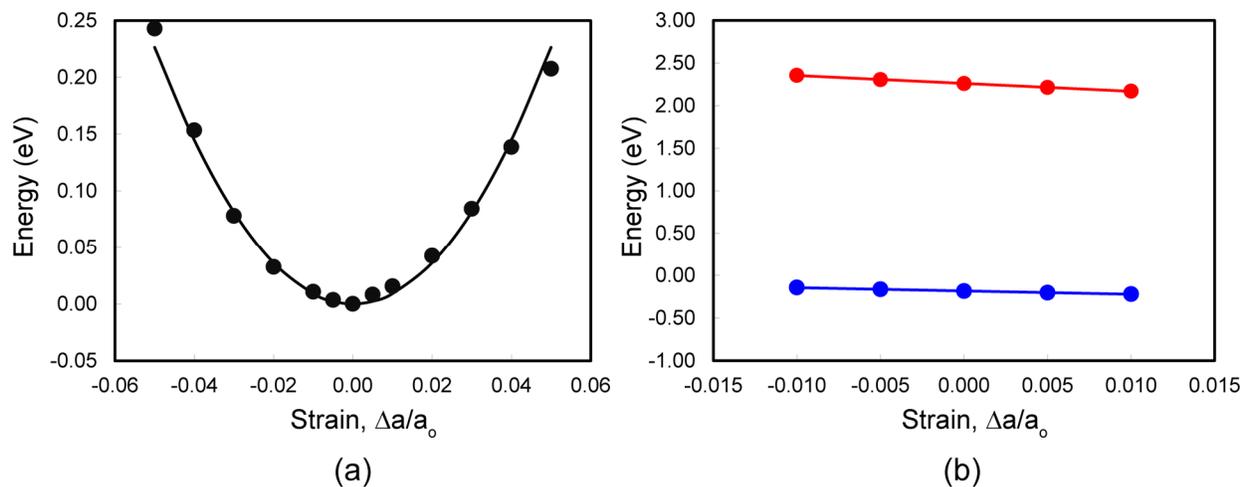


Figure S5. Relative energy per unit cell (a) and the shift of VB (blue) and CB (red) at K point (b) with respect to the strain along the a direction of single-layer MoS₂. The dots are the calculated values and the solid curves are fitted to the calculated data to determine DP constant E_1 , and in-plane stiffness C .

Table S4. DP constant E_1 , in-plane stiffness C_{2D} , effective mass and intrinsic charge mobility for single-layer MoS₂

	E_1 (eV)	C_{2D} (J/m ²)	m^* (m_e)	μ , cm ² /Vs
Electron	-9.21	160.04	0.48	116.94
Hole	-3.85	160.04	0.60	421.74

Section S7: Intrinsic Charge Mobility Calculation for Single-layer NiPc-P, NiPc-2P, and NiPc-3P

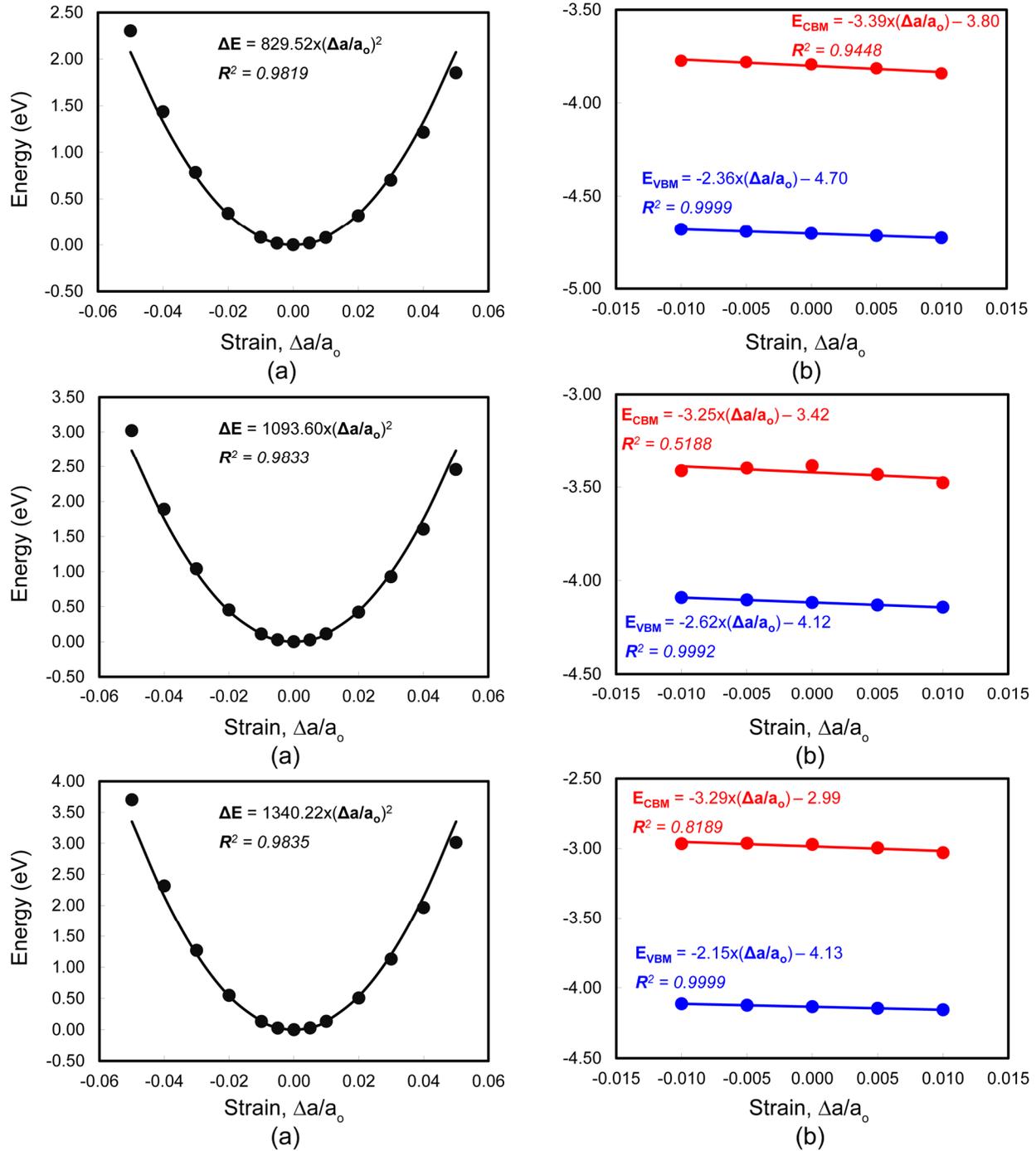


Figure S6. Relative energy per unit cell (left) and the shift of VBM and CBM (right) with respect to the strain along the a direction of single-layer NiPc-P (a, b), NiPc-2P (c, d), and NiPc-3P (e, f). The fitting curves and the coefficient of determination (R^2) are also shown.

Table S5. DP constant E_1 , in-plane stiffness C_{2D} , effective mass for single-layer NiPc-P, NiPc-2P, NiPc-3P

		E_1 (eV)	C_{2D} (J/m ²)	m^* (m_e)
NiPc-P	Electron	-3.39	236.97	1.08
	Hole	-2.36	236.97	0.10
NiPc-2P	Electron	-3.25	206.08	0.82
	Hole	-2.62	206.08	0.13
NiPc-3P	Electron	-3.29	179.18	0.60
	Hole	-2.15	179.18	0.16

Table S6. Effective mass along M- Γ for single-layer NiPc-P, NiPc-2P, NiPc-3P

		m^* (m_e)
NiPc-P	Electron	0.36
	Hole	0.09
NiPc-2P	Electron	0.31
	Hole	0.12
NiPc-3P	Electron	0.30
	Hole	0.14

Section S8: Intrinsic Charge Mobility Calculation for One-dimensional structures of NiPc-P, NiPc-2P, and NiPc-3P

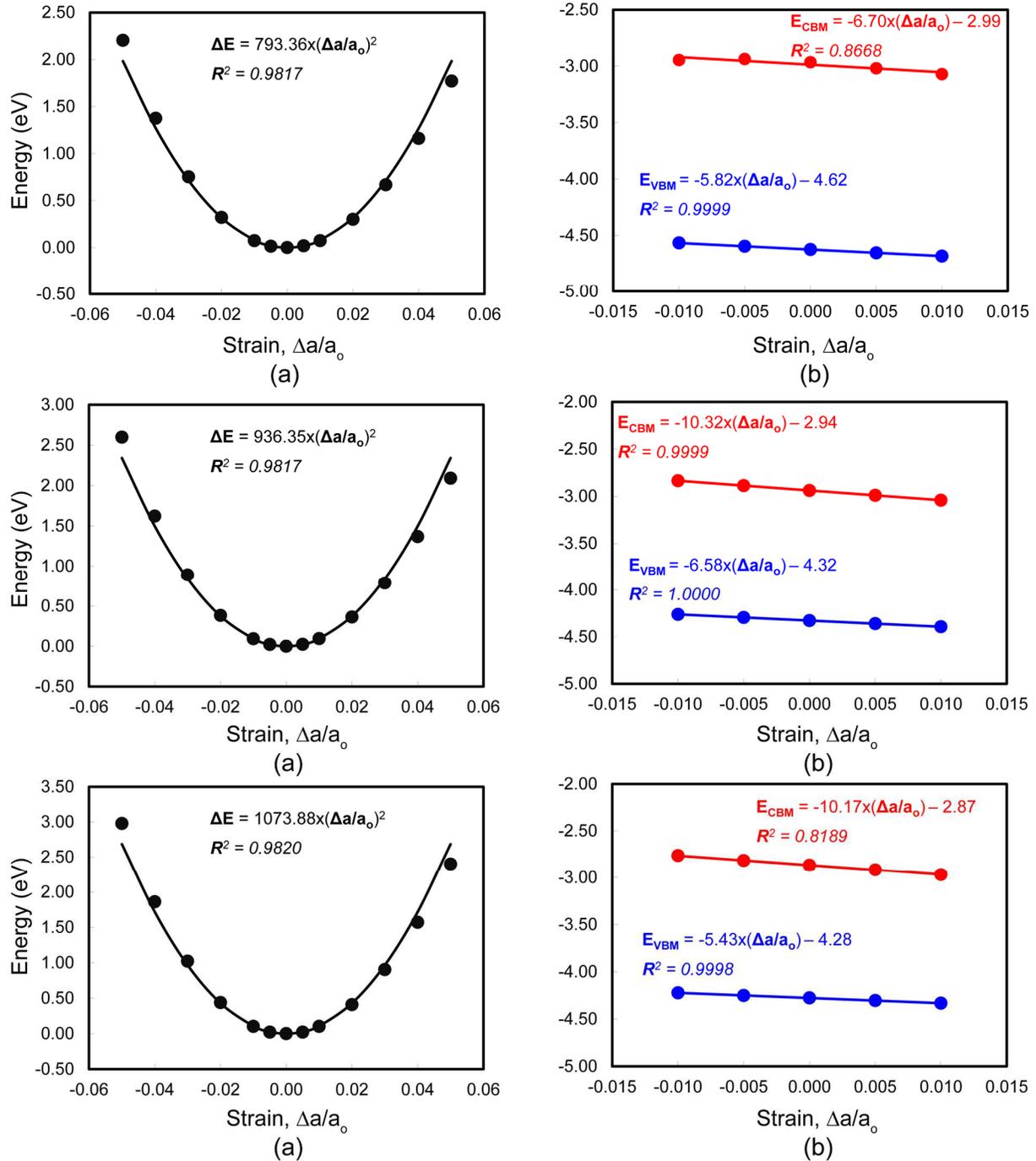


Figure S9. Relative energy of one unit cell (left) and the shift of VBM and CBM (right) with respect to the strain along the a direction of one dimensional structures of NiPc-P (a, b), NiPc-2P (c, d), and NiPc-3P (e, f). The fitting curves and the coefficient of determination (R^2) are also shown.

Table S7. DP constant E_1 , in-plane stiffness C_{1D} , effective mass, and intrinsic charge mobility for NiPc-P, NiPc-2P, NiPc-3P ribbons

		E_1 (eV)	C_{1D} (10^{-7} J/m)	m^* (m_e)	μ , cm^2/Vs
NiPc-P	Electron	-6.70	2.40	0.28	181.27
	Hole	-5.82	2.40	0.15	619.09
NiPc-2P	Electron	-10.32	2.30	0.85	13.58
	Hole	-6.58	2.30	0.15	464.75
NiPc-3P	Electron	-10.17	2.22	0.73	17.04
	Hole	-5.43	2.22	0.14	683.86

Section S9: In-plane stiffness Calculation for Graphene and Pc-P

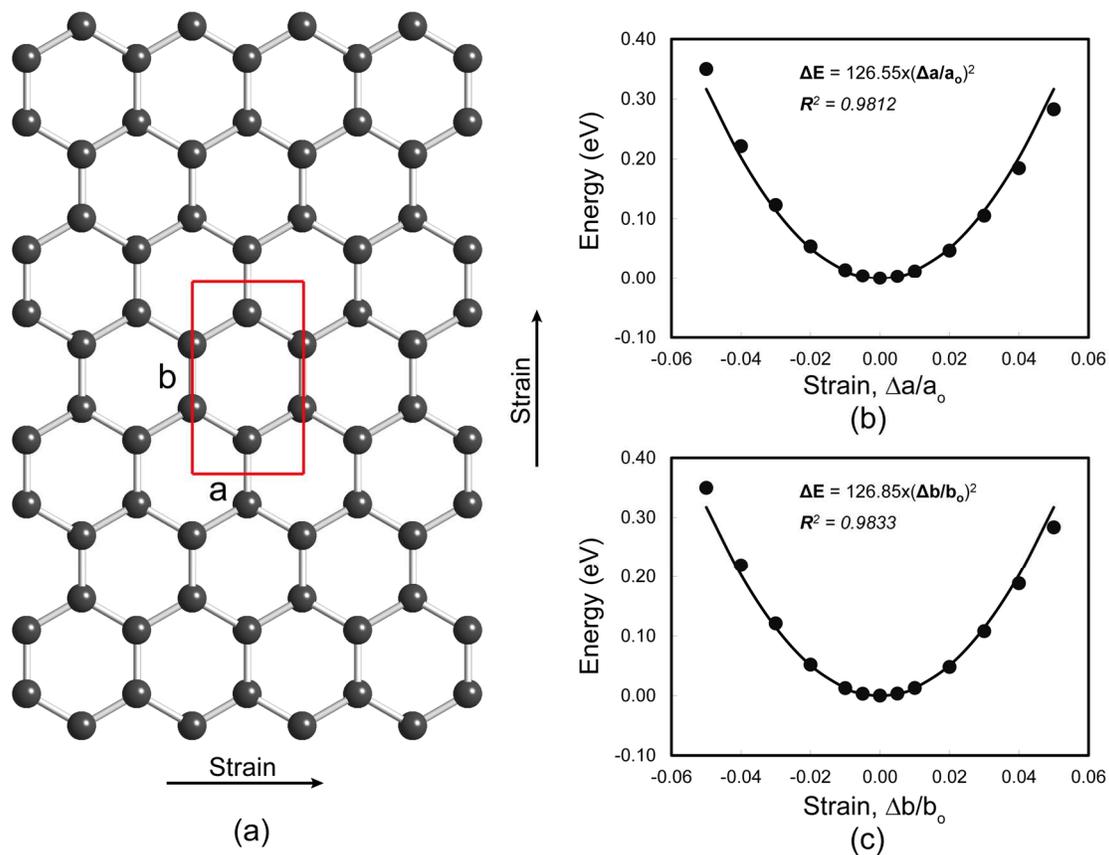


Figure S10. Single-layer structure of Graphene in the orthogonal unit cell (a) and the relative energy of one unit cell with respect to the strain along the a direction (b) and respect to the strain along the b direction (c).

Table S8. Calculated geometry and in-plane stiffness C_{2D} for Graphene

Lattice constants	a	2.452 Å
	b	4.246 Å
In-plane stiffness	a direction	389.56 J/m ²
	b direction	390.48 J/m ²

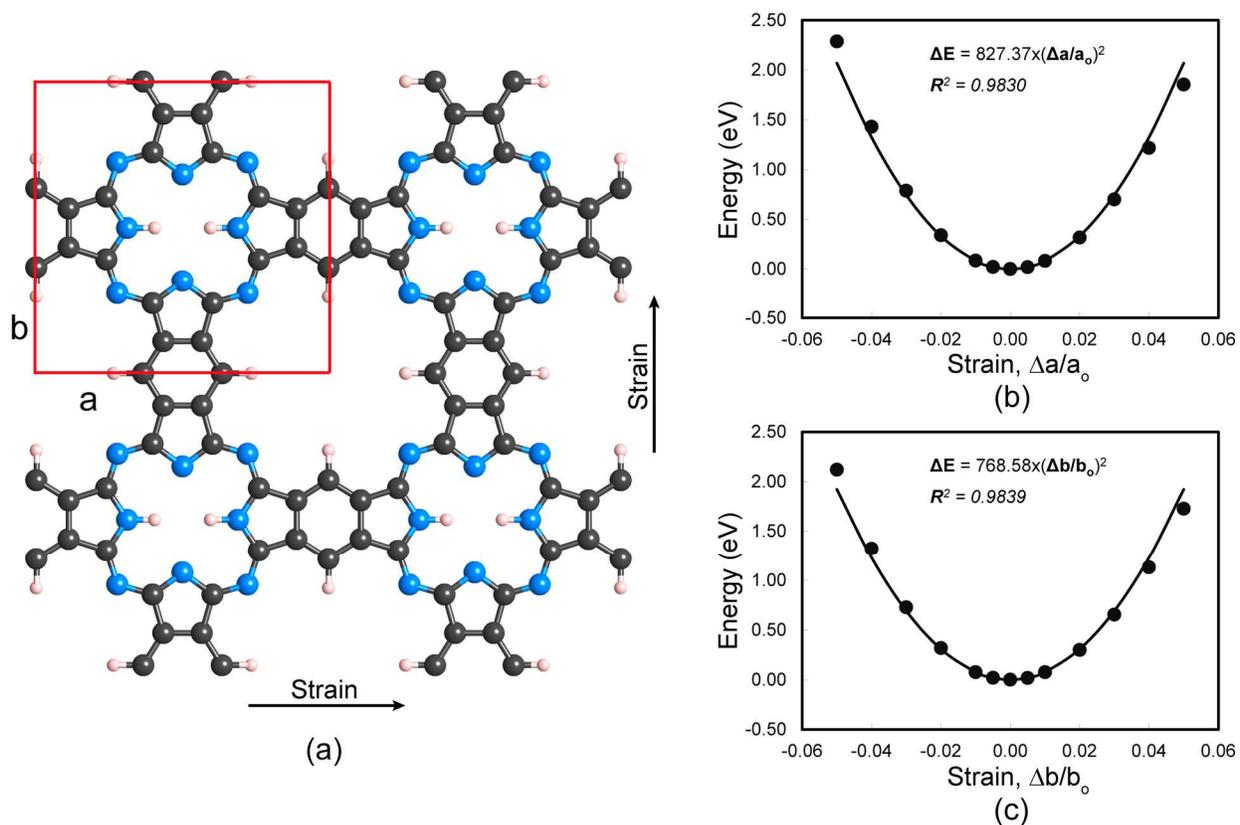


Figure S11. Single-layer structure of Pc-P (a) and the relative energy of one unit cell with respect to the strain along the a direction (b) and respect to the strain along the b direction (c). Atom colors: C, grey; N, blue; H, pink.

Table S9. Calculated geometry and in-plane stiffness C_{2D} for Pc-P

Lattice constants	a	10.683 Å
	b	10.664 Å
In-plane stiffness	a direction	232.72 J/m ²
	b direction	216.18 J/m ²

Reference

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2. J. Xi, M. Long, L. Tang, D. Wang and Z. Shuai, *Nanoscale*, 2012, **4**, 4348.
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6. R. Fivaz and E. Mooser, *Phys. Rev.*, 1967, **163**, 743.