Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Isolated Flat Bands and Physics of Mixed Dimensions in a 2D Covalent Organic Framework

Juefan Wang[1,2], Su Ying Quek[1,2,]*

[1]Department of Physics, National University of Singapore, 2 Science Drive 3, 117551, Singapore

[2]Centre for Advanced 2D Materials, National University of Singapore, Block S14, Level 6, 6 Science Drive 2, 117546, Singapore

Methods

The thermoelectric properties of 2D-CAP were studied based on DFT and Boltzmann transport theory [1]. DFT calculations were performed within the projector augmented-wave formalism [2] as implemented in the Vienna ab initio simulation package (VASP) [3]. The generalized gradient approximation [4] was used for the exchange-correlation functional. A plane-wave basis set with a kinetic energy cutoff of 550 eV was employed. The Brillouin zone was sampled on a 4 × 4 × 1 Monkhorst-pack grid for the self-consistent field calculation and a denser k grid of 20 × 20 × 1 for the non-self-consistent field calculation to obtain the Kohn-Sham energies for computing the Seebeck coefficients. Seebeck coefficients were calculated by means of Boltzmann semiclassical theory, within the constant relaxation time approximation, using the BoltzTraP2 code [5].

The on-site Coulomb interaction U at the bridge sites is estimated following Ref. [6]. The Coulomb interaction U is given by $U=\frac{e^2}{4\pi\varepsilon\epsilon_0 d}$, where the in-plane dielectric constant of 2D-CAP, ε, is computed from density-functional-perturbation-theory, with a value of 3.1. d is estimated by first obtaining the macroscopic planar-average of the localized wavefunction charge density $|\psi(r)|^2$, and d is the full-width-half-maximum of this function. The value of d is 6.4 Å. Our computed U = 730 meV.

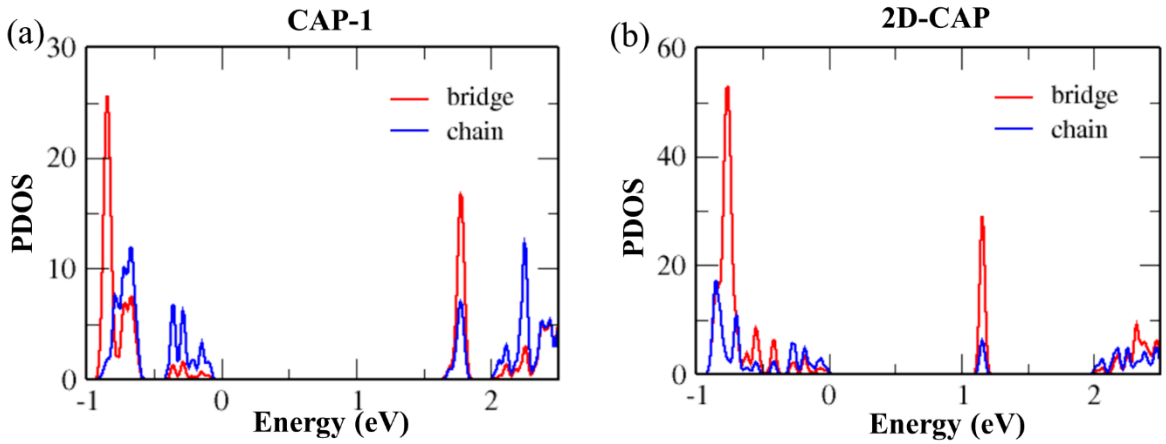

Figure S1. The calculated projected density of states (PDOS) of (a) monolayer CAP-1 and (b) monolayer 2D-CAP. The PDOS plots are obtained with a Gaussian broadening of 0.03 eV.

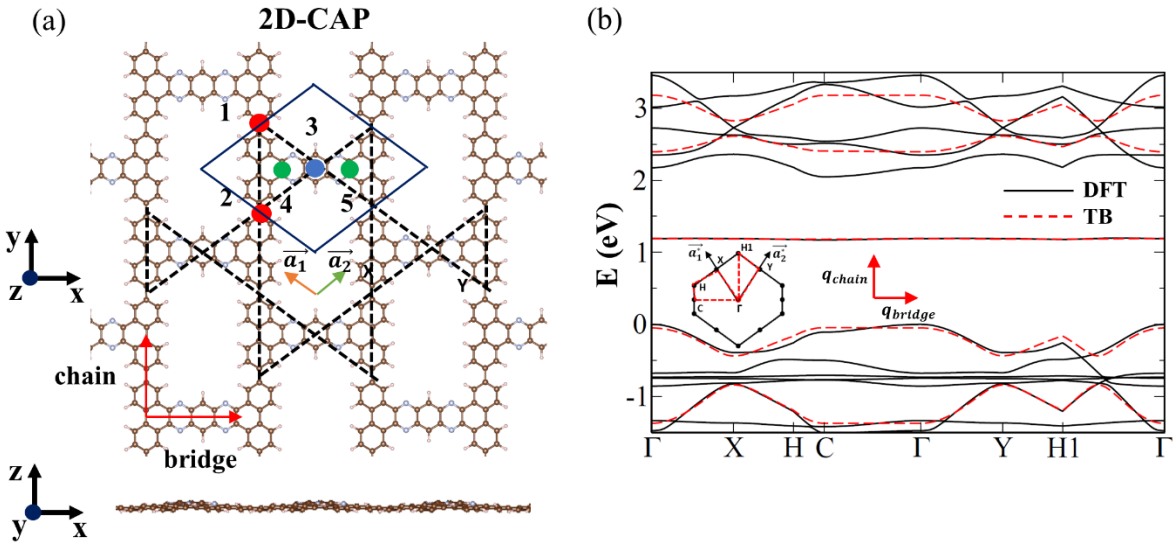

Figure S2. (a) The Kagome-honeycomb tight-binding (TB) model for monolayer 2D-CAP. The three Kagome sites are labelled as 1, 2 and 3, respectively. The two honeycomb sites are labelled as 4 and 5, respectively. (b) Band structure of 2D-CAP from DFT (black solid line) and TB model (red dashed line). The fitting parameters are shown in Table S1.

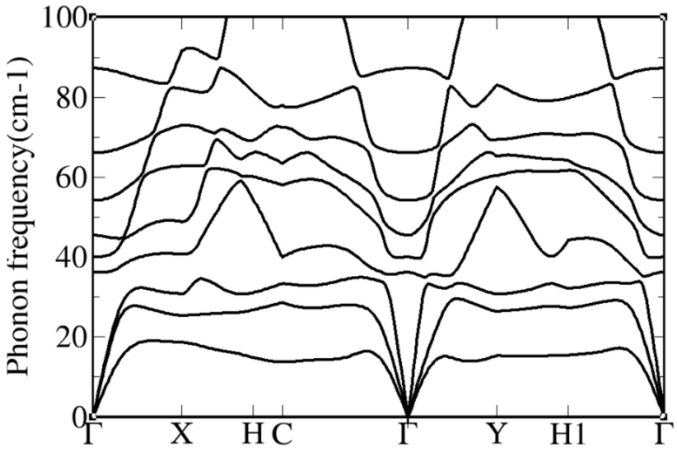

Figure S3. Phonon band structure of monolayer 2D-CAP.

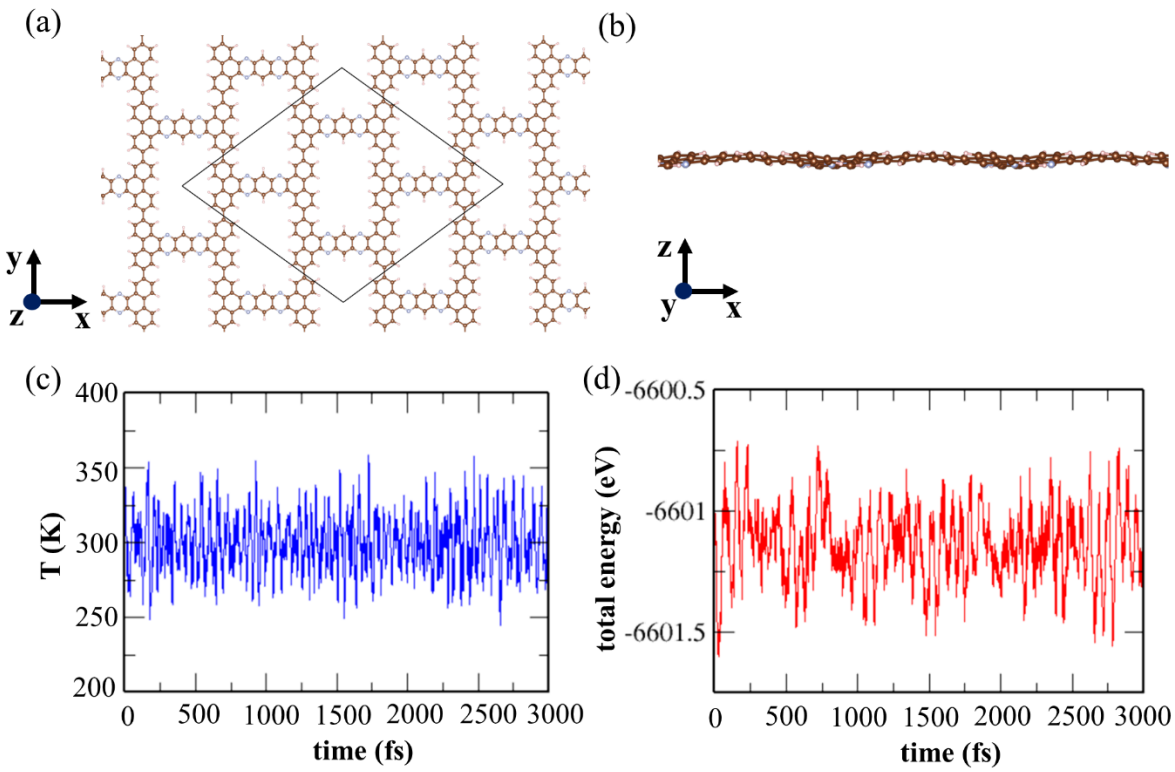

Figure S4. *Ab initio* molecular dynamics (MD) simulations of monolayer 2D-CAP at 300 K. (a) Top view and (b) side view of the constructed 2×2 supercell containing four primitive cells for MD simulation. The supercell is indicated by the black parallelogram. (c) Variation of temperature T (K) with respect to time iteration (fs). (d) Variation of total energy (eV) per primitive cell with respect to time iteration (fs).

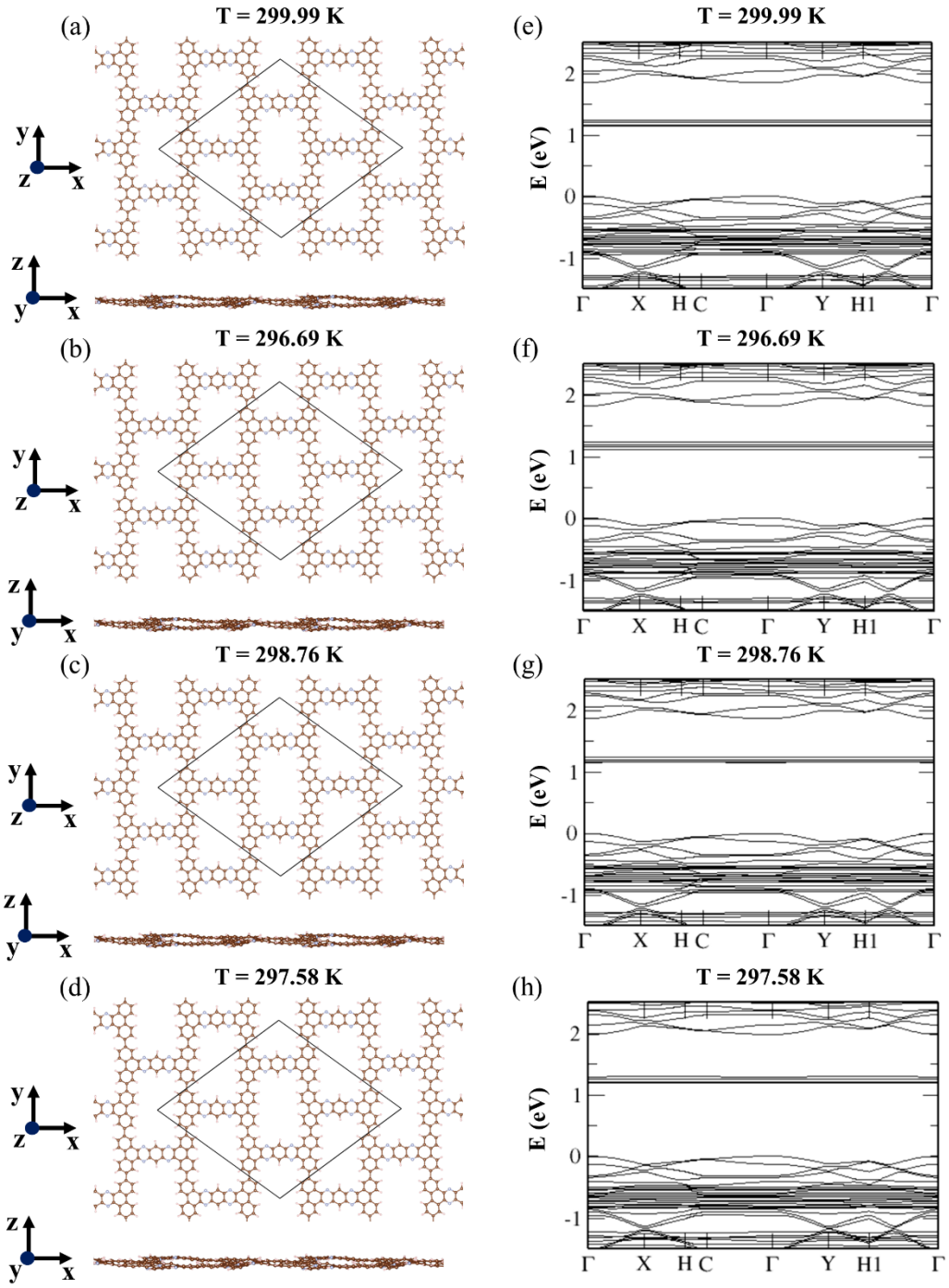

Figure S5. Snapshots of the (a-d) atomic structures and (e-h) band structures of monolayer 2D-CAP in the molecular dynamics simulation.

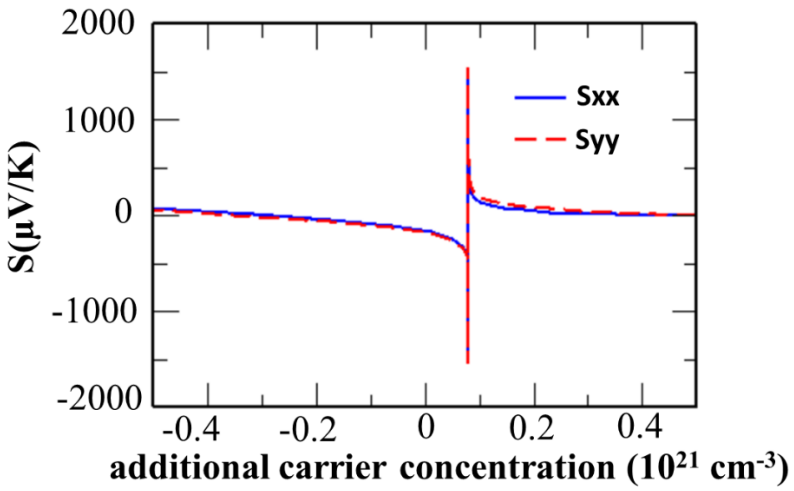

Figure S6. Seebeck coefficients (μV/K) computed at 300 K, as a function of carrier concentration (10^{21}cm^{-3}) of 2D-CAP doped with 0.2 e$^-$. The simulation illustrates that spin polarization does not have a significant effect on the Seebeck coefficients, and that the rigid band approximation, used in Figure 4, works reasonably well. Directions x and y correspond to the 'bridge' and 'chain' directions, respectively. S_{yy} is slightly larger than S_{xx} because of the asymmetry in the band dispersions in the valence band.

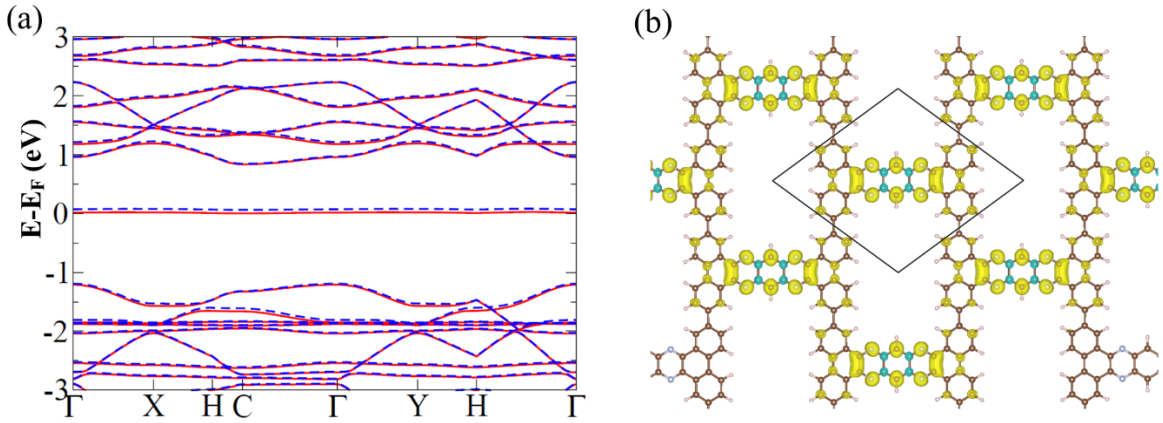

Figure S7. Electronic structure of 2D-CAP doped with 0.2 electrons. (a) Spin-polarized band structure. Red solid lines: majority spin, blue dashed lines: minority spin. (b) The corresponding spin density plot. The majority spin and minority spin density are indicated by yellow and green, respectively. The isosurface value is 5% of the maximum.

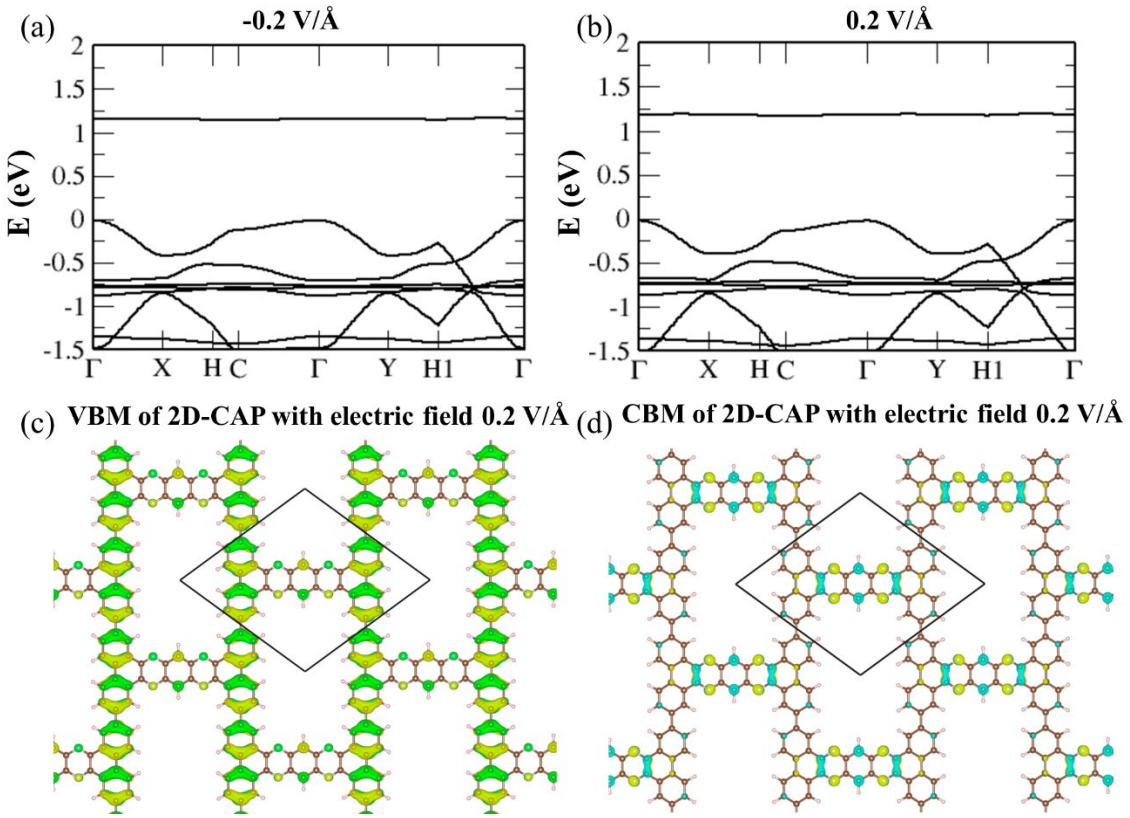

Figure S8. Electronic structure of monolayer 2D-CAP after applying electric fields. Band structure of monolayer 2D-CAP with electric field of (a) -0.2V/Å (b) 0.2V/Å. Gamma point Kohn-Sham wave functions for (c) VBM and (d) CBM of 2D-CAP. Isosurface values are chosen to be 10 % of the maximum value in each case. Positive and negative values are indicated by green and yellow, respectively.

Table S1. Optimized tight-binding parameters (in eV) for monolayer 2D-CAP using a Kagome-honeycomb lattice model. The on-site energies of each site are indicated by ε_i (i from 1 to 5). For the hopping terms, we use the following notations - $t_1 = t_{12}(t_{21})$: hopping between Kagome site 1 and site 2; $t_2 = t_{13}(t_{31}) = t_{23}(t_{32})$: hopping between Kagome site 1/2 and Kagome site 3; $t_3 = t_{14}(t_{41}) = t_{15}(t_{51}) = t_{24}(t_{42}) = t_{25}(t_{52})$: hopping between Kagome site 1/2 and honeycomb site 4/5; $t_4 = t_{34}(t_{43}) = t_{35}(t_{53})$: hopping between Kagome site 3 and honeycomb site 4/5; $t_5 = t_{45}(t_{54})$: hopping between honeycomb site 4 and honeycomb site 5.

on-site energy(eV)	$\boldsymbol{\varepsilon_1}$	$\boldsymbol{\varepsilon_2}$	$\boldsymbol{\varepsilon_3}$	$\boldsymbol{\varepsilon_4}$	$\boldsymbol{\varepsilon_5}$
	-0.55	-0.11	1.20	2.29	2.52
hopping term (eV)	$\boldsymbol{t_1}$	$\boldsymbol{t_2}$	$\boldsymbol{t_3}$	$\boldsymbol{t_4}$	$\boldsymbol{t_5}$
	0.51	0.00	0.68	0.10	0.00

References:

1. Allen, P.B. *Boltzmann Theory and Resistivity of Metals*. 1996.
2. Blöchl, P.E., *Projector augmented-wave method.* Physical Review B, 1994. **50**(24): p. 17953-17979.
3. Kresse, G. and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.* Physical Review B, 1996. **54**(16): p. 11169-11186.
4. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple.* Physical Review Letters, 1996. **77**(18): p. 3865-3868.
5. Madsen, G.K.H., J. Carrete, and M.J. Verstraete, *BoltzTraP2, a program for interpolating band structures and calculating semi-classical transport coefficients.* Computer Physics Communications, 2018. **231**: p. 140-145.
6. Naik, M.H. and M. Jain, *Ultraflatbands and Shear Solitons in Moire Patterns of Twisted Bilayer Transition Metal Dichalcogenides.* Physical Review Letters, 2018. **121**(26): p. 266401.