### Supplementary Information

**Table S1.** Calculated equilibrium lattice constant ($a$, Å), bond length of Fe-I ($l_{Fe-I}$, Å), angle of the I-Fe-I ($\angle \alpha$, °), magnetic moment of Fe ($M$, $\mu_B$), cohesive energy ($E_{coh}$, eV/atom), and exchange energy with DFT+U and HSE functional, respectively ($E_{exc} = E_{AFM} - E_{FM}$, meV).

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$l_{Fe-I}$</th>
<th>$\angle \alpha$</th>
<th>$M$</th>
<th>$E_{coh}$</th>
<th>$E_{exc}$ (DFT+U)</th>
<th>$E_{exc}$ (HSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$I$_2$</td>
<td>3.81</td>
<td>2.68</td>
<td>90.34</td>
<td>~3</td>
<td>3.01</td>
<td>516</td>
<td>478</td>
</tr>
</tbody>
</table>

**Figure S1.** (a) Electron localization function (ELF); ELF = 1.0 (red) and 0.0 (blue) indicate accumulated and vanishing electron density, respectively. (b) Harmonic phonon analysis of SL Fe$_2$I$_2$. (c) Snapshot of SL Fe$_2$I$_2$ at the end of MD simulation at 500 K after 10 ps. (d) Changes of the total energy with the trajectory time, obtained from MD simulations of SL Fe$_2$I$_2$ at 500 K.
Figure S2. (a) Calculated cohesive energy ($E_{coh}$, eV/atom) for a wide range of 2D Fe$_x$I$_y$ binary materials where the insets show their corresponding crystal structures. The 1T’-FeI$_2$ and P-Fe$_2$I$_2$ structures, denoted by the horizontal black arrows, undergo structural phase transitions to the 1T-FeI$_2$ and S-Fe$_2$I$_2$ structures, respectively, after geometry relaxation. (b) Calculated phonon dispersion curves of the proposed 2H-FeI$_2$. (c) Minority (Orange line) and majority (blue line) spin-resolved band structure of the 2H-FeI$_2$ layer. (d) and (e) Phonon dispersion curves of the proposed G-FeI, and Si-FeI layers, respectively.

In order to determine the ground state of the 2D Fe$_x$I$_y$ binary materials, we have constructed seven additional possible configurations based on the conventional prototypes of 2D material family. As shown in Figure S2, these additional 2D Fe$_x$I$_y$ crystals include the graphene-like FeI (denoted as G-FeI), silicene-like FeI (Si-FeI), phosphorene-like FeI (P-Fe$_2$I$_2$), 1T-MoS$_2$-like FeI$_2$ (1T-FeI$_2$), CrI$_3$-like FeI$_3$ (C-FeI$_3$), 1T’-WTe$_2$-like FeI$_2$ (1T’-FeI$_2$), and 2H-MoS$_2$-like FeI$_2$ (2H-FeI$_2$). Overall, the calculations reveal several important results: (1) the square Fe$_2$I$_2$ single-layer (SL) (shown in this work, denoted as S-Fe$_2$I$_2$) is indeed the ground state with the highest $E_{coh}$. (2) Similar to the reported 1T-FeI$_2$ $^{[1-3]}$, the 2H-FeI$_2$ SL shows an insulating electronic behavior and in-plane
magnetic orientation (MCA = -1.98 meV) with a dynamically stable crystal structure. (3) The 2D G-FeI and Si-FeI hexagonal structures are not stable because of the emergence of imaginary frequencies in the phonon spectra.

![Figure S3. The magnetic moments variation of the Fe atom as functions of temperature by means of Monte Carlo simulations on the basis of 2D Heisenberg Hamiltonian model.](image)

**Figure S3.** The magnetic moments variation of the Fe atom as functions of temperature by means of Monte Carlo simulations on the basis of 2D Heisenberg Hamiltonian model.

![Figure S4. The variation of MCA and orbital moment anisotropy verse strain effect for Fe₂I₂ SL.](image)

**Figure S4.** The variation of MCA and orbital moment anisotropy verse strain effect for Fe₂I₂ SL.
Figure S5. The SOC-induced energy gap of the 2D Fe$_2$I$_2$ crystal as a function of biaxial strain effect.

Figure S6. Band structure of the edges of Fe$_2$I$_2$ ribbon as a function of in-plane lattice constants (a) 3.992 Å (4.65%), (b) 3.924 Å (3%), (c) 3.696 Å (-3%) and (d) 3.620 Å (-5%) with robust edge states, denoted by green, connecting the 2D valence and conduction bands.
Figure S7. The proposed Fe$_2$I$_2$/BTO junctions consisting of Fe$_2$I$_2$ SL on five unit cells of BaTiO$_3$. Blue, orange, green, gray and red spheres denote the Fe, I, Ba, Ti, and O atoms, respectively. The gray arrows show the polarization directions.

Figure S8. The Fe$_2$I$_2$ layer-resolved band structure for the three different Fe$_2$I$_2$/BTO configurations, i.e. $C_G^\downarrow$ (left panel), $C_M^\uparrow$ (central panel), and $C_G^\uparrow$ (right panel, respectively).
The SOC energy difference is defined as \( \Delta E_{\text{SOC}} = (E_{\text{SOC}}^\rightarrow - E_{\text{SOC}}^\uparrow) / 2 \), where

\[
\Delta E_{\text{SOC}} = \frac{\hbar^2}{2m^2c^2} \left\langle \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{S} \right\rangle \\
= \sum_{I,lm;\sigma,\sigma'} \xi_0 (Ilm\sigma|\vec{L} \cdot \vec{S}|Ilm'\sigma') \rho_{lm',\sigma\sigma'}^{II}
\]

Here, \( \rho_{lm',\sigma\sigma'}^{II} = \frac{1}{N_k} \sum_{nk} \langle Ilm'\sigma'|nk\rangle \langle nk| Ilm\sigma \rangle f(\varepsilon_{nk}) \), where \( I \) is the atomic index, \( lm \) are the angular momentum orbitals, \( \sigma, \sigma' \) is the spin index, \( \xi_0 \) is the atomic SOC strength obtained from the spherical part of the effective potential, \( V(r) \), within the PAW sphere, \( \rho_{lm',\sigma\sigma'}^{II} \) is the density matrix projected on atomic orbitals, \( \vec{L} \) and \( \vec{S} \) are the orbital and spin operators, respectively.

low-energy effective Hamiltonian:

In the absence of SOC, the 2D Fe\(_2\)I\(_2\) SL hosts two pair of Dirac points along the \( k_x \) and \( k_y \) axes, locating at \((\pm k_0, 0)\) and \((0, \pm k_0)\), respectively. We have constructed the low-energy effective \( k \cdot p \) Hamiltonian to describe the Dirac cones, for instance, for the ones denoted as \( D_1 \) (\( D_2 \)) at \((k_0, 0)\) (\((0, k_0)\)). At \( D_1 \) (\( D_2 \)), the two relevant bands forming the Dirac point are labeled as \( \phi_1 \) and \( \phi_2 \).

Under basis \( \Psi = (\phi_1, \phi_2)^T \), the Hamiltonian can be expressed as

\[
H_{D_1}(p_x, p_y) = p_x \sigma_1 + p_y (\lambda_1 \sigma_1 + \lambda_2 \sigma_2) \\
H_{D_2}(p_x, p_y) = p_x \sigma_1 + p_y (\lambda_1 \sigma_1 + \lambda_2 \sigma_2), \quad (\text{Eq. SI})
\]

where \( \sigma_{1,2,3} \) are the Pauli Matrices and \( \lambda_{1,2} \) are real constants.
References: