Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Tailoring interlayer magnetic coupling to modify magnetic properties of $FeCl_2$ bilayer by self-intercalation

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Table S1 Lattice constant a (Å), interlayer distance d (Å), bond length $d_{\text{Fe-Cl}}$ (Å) of Fe-Cl, bond angle θ_1 (^{o}) of Cl-Fe-Cl, θ_2 (^{o}) of Fe-Cl-Fe, formation energy E_f (eV) and magnetic ground state of $FeCl_2$ bilayer.

a	d	$d_{\text{Fe-Cl}}$	θ_1	θ_2	E_f	Magnetic ground
3.507	3.0667	2.459	89.132	90.750	-0.895	AFM

Table S2 Neighboring number of exchange constants in self-intercalated $FeCl_2$ bilayer with different concentrations.

	11%	25%	33%	67%	100%
J_{intra1}	108	48	36	36	12
J_{inter1}	18	8	6	6	2
J_{intra2}	6	6	6	6	6
J_{inter2}	4	4	4	8	4

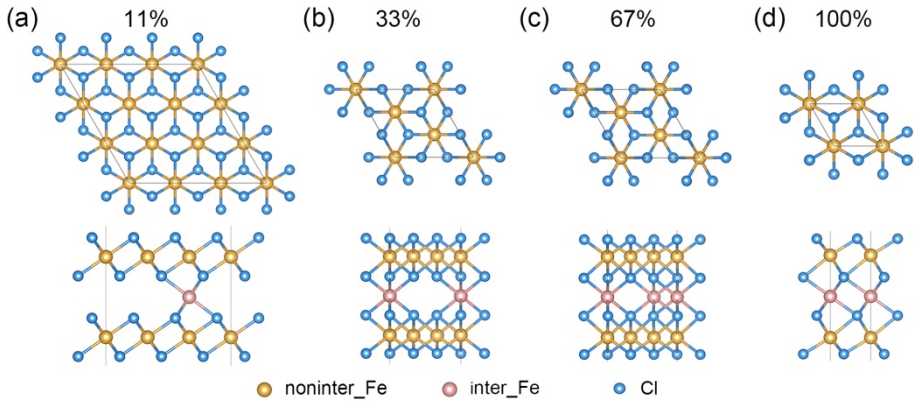

Fig. S1 Top and side views of Fe-intercalated $FeCl_2$ bilayer with concentration of (a) 11%, (b) 33%, (c) 67% and (d) 100%.

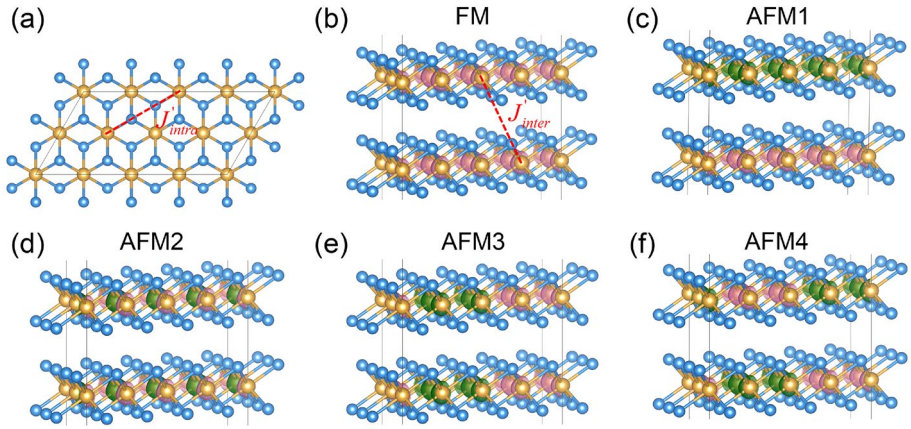

Fig. S2 (a) Top view of $FeCl_2$ bilayer of 2×4×1 supercell. (b)-(f) Spin charge density of five different magnetic configurations. Pink and green areas represent the opposite spin states. The isosurface is 0.070 e/Bohr^3.

The energy contributed by magnetic interaction in these magnetic orders in a unit cell can be expressed as

$$E_{FM} = E_0 - \left(6J_{intra} + 6J'_{intra} + J_{inter} + 6J'_{inter}\right)S^2 \quad \text{(S1)}$$

$$E_{AFM1} = E_0 - \left(6J_{intra} + 6J'_{intra} - J_{inter} - 6J'_{inter}\right)S^2 \quad \text{(S2)}$$

$$E_{AFM2} = E_0 + \left(2J_{intra} + 2J'_{intra} - J_{inter} + 2J'_{inter}\right)S^2 \quad \text{(S3)}$$

$$E_{AFM3} = E_0 - \left(2J_{intra} - 2J'_{intra} + J_{inter} + 2J'_{inter}\right)S^2 \quad \text{(S4)}$$

$$E_{AFM4} = E_0 - \left(2J_{intra} - 2J'_{intra} - J_{inter} - 2J'_{inter}\right)S^2 \quad \text{(S5)}$$

Here, J_{intra} and J_{inter} are the nearest-neighbor exchange constants of intralayer and interlayer, In Fig.

S1a and b, J'_{intra} and J'_{inter} are the second-nearest-neighbor exchange constants. The J>0 denotes the ferromagnetic order, while the J<0 represents the antiferromagnetic order. To investigate the contributions from more distant interaction, the second-nearest-neighbor exchange interaction are included in $FeCl_2$ bilayer. The J_{intra}, J_{inter}, J'_{intra} and J'_{inter} are 5.117, 0.241, -0.227 and -0.111 meV, respectively. The second-nearest-neighbor exchange constants are smaller than the nearest-neighbor exchange constants, so the second-nearest-neighbor magnetic coupling will not be considered in this work.

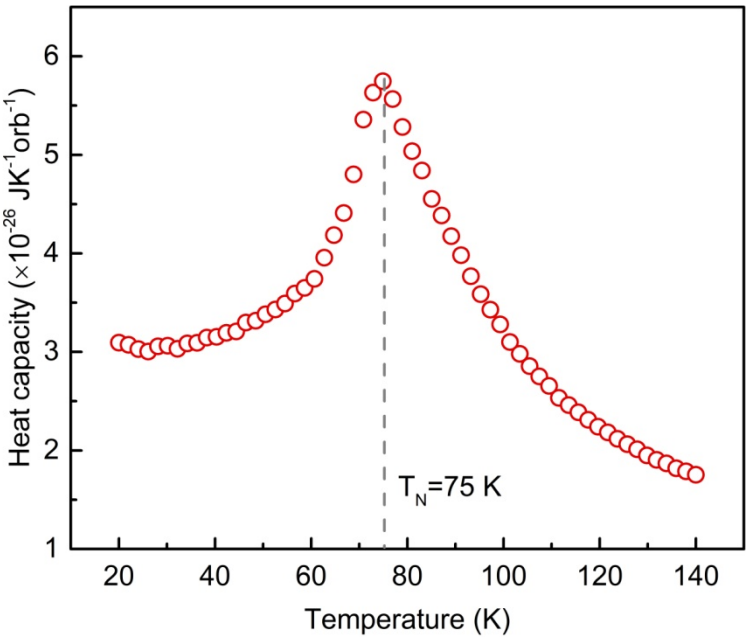

Fig. S3 Specific heat capacity as a function of temperature of the $FeCl_2$ bilayer.

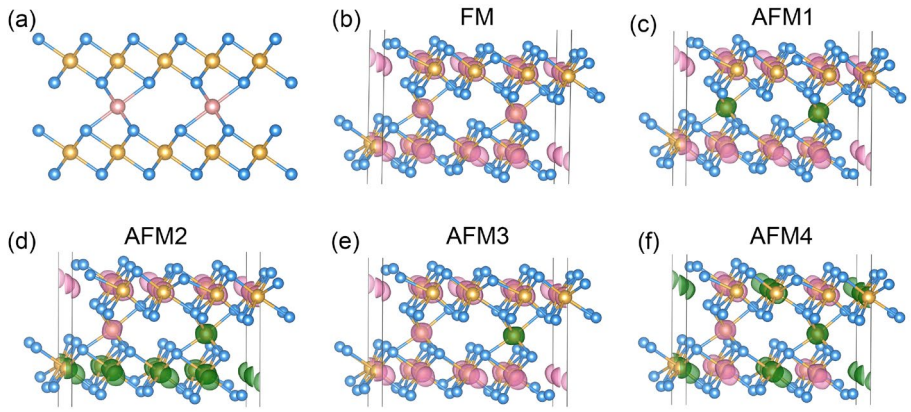

Fig. S4 (a) Side view of 25% Fe-intercalated $FeCl_2$ bilayer. The red dash lines represent the exchange interaction between Fe sites. (b)-(f) Spin charge density of five different magnetic configurations. Pink and green areas represent the opposite spin states. The isosurface is 0.070 e/Bohr^3.

The energy contributed by magnetic interaction in these magnetic orders in a unit cell can be expressed as

$$E_{FM} = E_0 - \left(12J_{intra1} + \frac{3}{2}J_{inter1} + J_{intra2} + \frac{3}{2}J_{inter2}\right)S^2 \tag{S6}$$

$$E_{AFM1} = E_0 - \left(12J_{intra1} + \frac{3}{2}J_{inter1} - J_{intra2} + 2J_{inter2}\right)S^2 \tag{S7}$$

$$E_{AFM2} = E_0 - \left(12J_{intra1} - \frac{1}{2}J_{inter1} - 2J_{inter2}\right)S^2 \tag{S8}$$

$$E_{AFM3} = E_0 - \left(12J_{intra1} - \frac{1}{2}J_{inter1} + 2J_{inter2}\right)S^2 \tag{S9}$$

$$E_{AFM4} = E_0 + \left(4J_{intra1} + \frac{1}{2} J_{inter1} - 2J_{inter2} \right) S^2 \quad \text{(S10)}$$

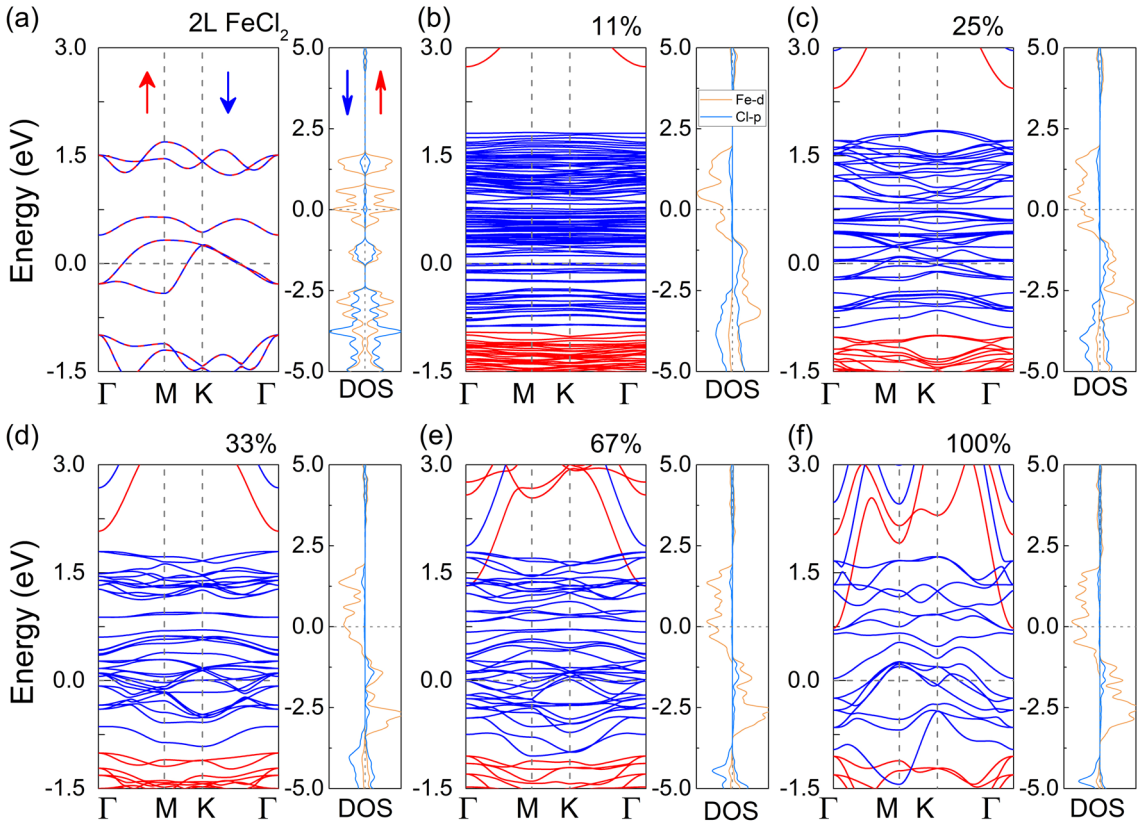

Fig. S5 Band structures and projected density of states of (a) $FeCl_2$ bilayer, (b) 11%, (c) 25%, (d) 33%, (e) 67% and (f) 100% Fe-intercalated $FeCl_2$ bilayer. The Fermi level is set at 0 eV.