Supporting Information

Towards Room-Temperature Magnetic Semiconductors in Two-Dimensional Ferrimagnetic Organometallic Lattice

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Computational Methods

First principles calculations are conducted within the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA)[1] with van der Waals interaction (vdW) correction using the DFT-D3 method[2,3] implemented in Vienna ab initio simulation package (VASP).[4] For structure optimization and test calculations, the PBE+U method[5] is used to treat the strong-correlation effect of transition metal's *3d* electrons, with Coulomb interaction parameter (U) and exchange interaction parameter (J) set to 4.0 and 1.0 eV, respectively.[6] To obtain accurate magnetic and electronic properties, the hybrid HSE06 functional is employed.[7,8] The projector augmented wave (PAW) potential[9] and the plane-wave cut-off energy of 520 eV are used. k-point meshes of 4×4×1 and 6×6×1 in the Monkhorst-Pack scheme are adopted during structure optimization and property calculation, respectively. Both the lattice constants and positions of all atoms are relaxed until the force is less than 0.01 eV/Å. The criterion for the total energy is set as 1×10^{-5} eV. To investigate the stability of DPP based organometallic frameworks, using PBE+U functional, phonon band structure is computed by the Phonopy package,[10] and ab initio molecular dynamics (AIMD) which last for 16 ps are performed in NVT ensemble at different temperatures (300 and 400 K) with a timestep of 1 fs.

Figures S1-S6

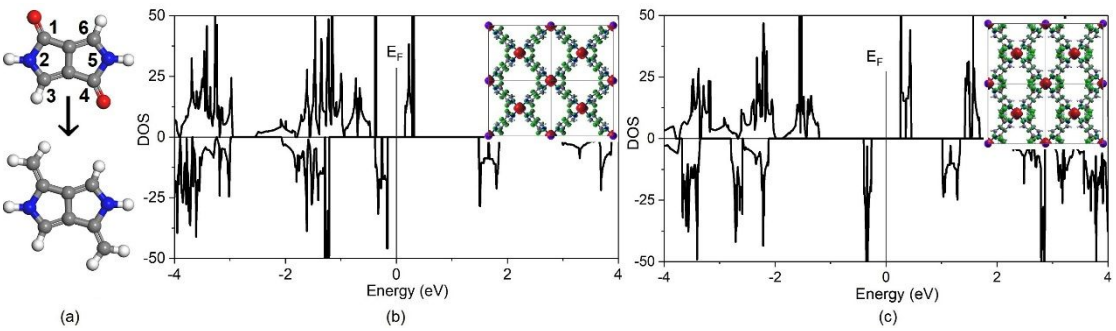

Figure S1. Test calculations of 2D Cr-DPP without and with methylene protection at PBE+U level. (a) is the scheme of replacing =O with isoelectronic $=CH_2$. (b)-(c) are the density of states for 2D Cr-DPP before and after methylene protection, respectively. Insets are the spin density for ground ferrimagnetic state with an isovalue of 0.05 e/Å^3. Fermi levels are set to

zero. One can find that the density of states around the Fermi level in (b)-(c) resemble each other with similar spin distribution.

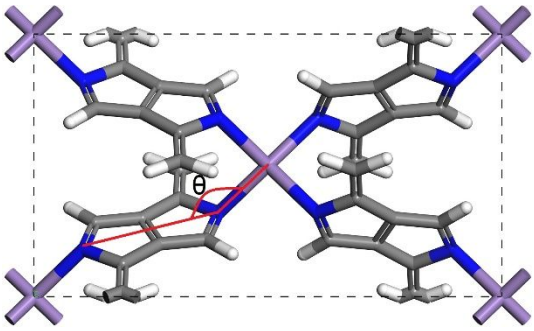

Figure S2. Optimized structure of 2D Mn-DPP. The Cr-N bond significantly deviates from the DPP plane with an angle about 140°.

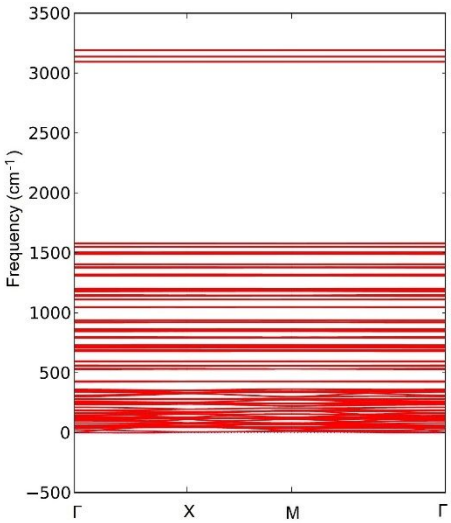

Figure S3. Phonon band structure of 2D Cr-DPP.

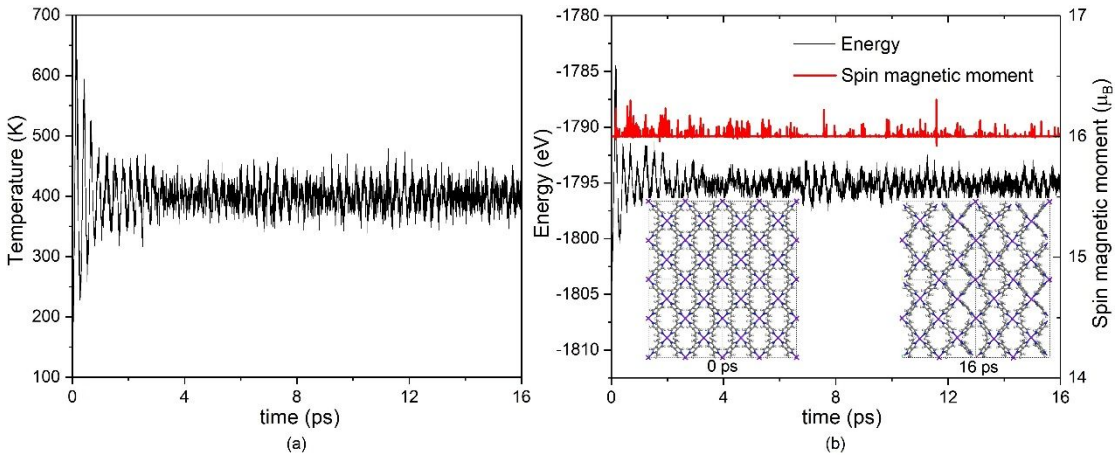

Figure S4. Ab initio molecular dynamics (AIMD) at 400 K for 2D Cr-DPP at PBE+U level. (a)-(b) are the fluctuation of temperature, energy and spin magnetic moment. Insets are the snapshots at 0 and 16 ps. No structure destruction is found, and 2D Cr-DPP is expected to stabilize at 400 K.

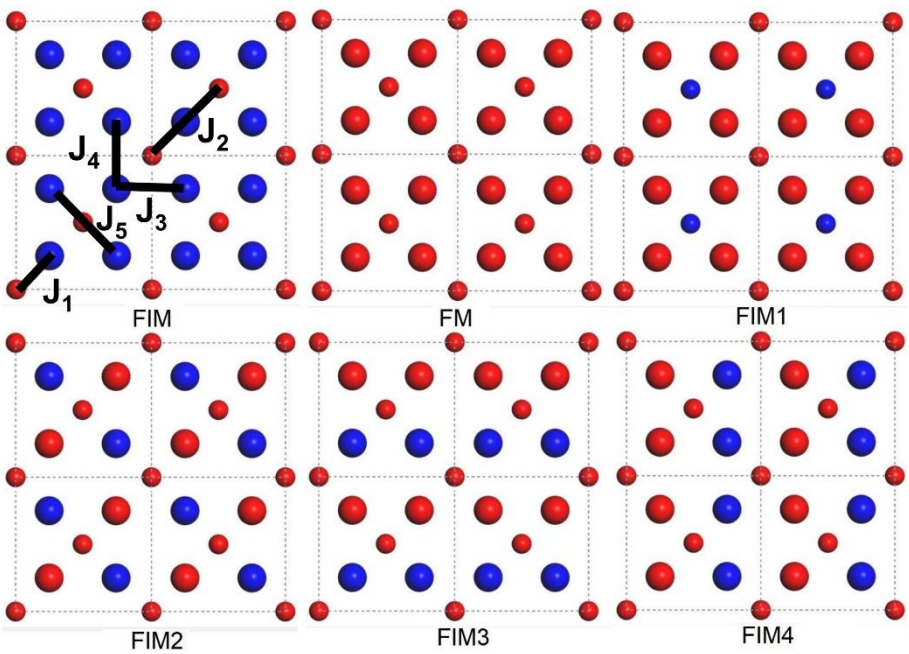

Figure S5. Computation of next-nearest and father exchange parameters for 2D Cr-DPP. Besides the nearest exchange parameter J_1, we consider other four exchange parameters J_2, J_3, J_4, J_5 as labeled in the figure. To get these values, other four ferrimagnetic states labelled as FIM1, FIM2, FIM3, FIM4 are calculated, which are found 149.9, 146.8, 150.0, 161.1 meV higher in energy than the ground FIM state. Accordingly, we obtain the exchange parameters J_2 = -0.4 meV, J_3 = -1.5 meV, J_4 = -7.1 meV and J_5 = 0.1 meV, being at least one order of magnitude smaller than J_1 (-20.5 meV).

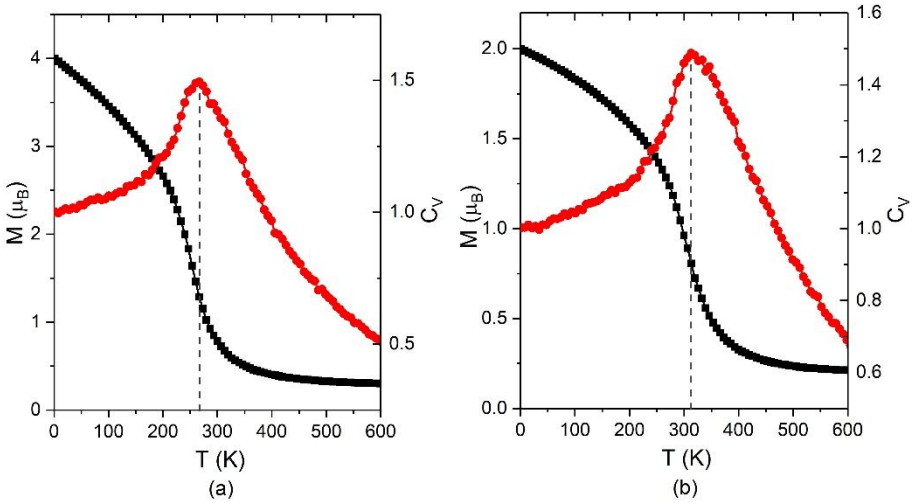

Figure S6. Variation of magnetic moment (M) per unit cell (black) and specific heat (C_V) (red) with respect to temperature from classic Heisenberg model Monte Carlo (MC) simulations for -CN modified 2D (a) Cr-DPP and (b) V-DPP at 5% compressive strain. The exchange energy is evaluated to be 1.002 and 1.209 eV, and the Curie temperature identified as the peak position of C_v plot is 270 and 310 K for modified 2D Cr and V-DPP, respectively.

Table S1. A list of theoretically predicted two dimensional intrinsic ferromagnetic semiconductors in the literature. The name/chemical formula, estimated Curie temperature (T_c), the method for predicting T_c, *i.e.* mean field theory (MFT), Ising model or classic Heisenberg model Monte Carlo simulation, and the reference number are given.

	T_c/K	method	reference
graphone	278	MFT	Ref. 11
$CrSnTe_3$	170	Ising	Ref.12
$CrGaTe_3$	71	Ising	Ref.13
$NiCl_2$	138	Ising	Ref.14
MnO_2	140	Ising	Ref.15
$MnSe_2$	250	Ising	Ref.16
CrOCl	160	Ising	Ref.17
CrSeBr	500	Ising	Ref.18
$CrWI_6$	180	Heisenberg	Ref.19
NbS_2	141	Heisenberg	Ref.20

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