

Magnet Design by Integration of Layer and Chain Magnetic Systems in a π -Stacked Pillared Layer Framework**

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Abstract: The control of inter-lattice magnetic interactions is a crucial issue when long-range ordered magnets that are based on low-dimensional magnetic frameworks are designed. A “pillared layer framework (PLF)” model could be an efficient system for this purpose. In this report, A magnet based on a π -stacked PLF with a phase transition temperature of 82 K, which can be increased to 107 K by applying a pressure of 12.5 kbar, is rationally constructed. Two types of low-dimensional magnetic framework systems, an electron donor/acceptor magnetic layer and a charge transfer $[\text{FeCp}^*_2]^+\text{TCNQ}^-$ columnar magnet ($[\text{FeCp}^*_2]^+$ = decamethylferrocenium; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane), are integrated to fabricate the magnet. This synthetic strategy employing a combination of layers and chains is widely useful not only for magnet design, but also for the creation of multifunctional materials with pores and anisotropic frameworks.

In the bottom-up synthesis of molecule-based long-range ordered magnets (abbreviated hereafter simply as magnets), the design of bonding frameworks that enable superexchange magnetic pathways is the first issue, followed by the control of exchange coupling between spins through the framework. Unlike for homogeneously constructed three-dimensional (3D; the dimensionality of the lattice) finite frameworks, in low-dimensional framework systems, including 1D chains and 2D layers, it is difficult to control the interchain or interlayer magnetic interactions, respectively, which are generally very weak, very often antiferromagnetic, and sometimes cause randomness owing to partial packing fluctuations. Consequently, this lack of control is often regarded as a disadvantage for the design of magnets with higher phase transition temperatures (T_C), although these interactions are of course crucial for the magnetic properties of these materials.

To control the magnetic ordering in a class of 2D layered compounds, we propose to use a pillared layer framework

(PLF) structural model, which is an anisotropic jungle-gym framework composed of layers and pillars. Recent work in molecular porous chemistry has led to the rational design of frameworks for the control of functionalities not only in the pores but also on the frameworks, and has resulted in significant advances in this field.^[1] The PLF is such a prototype framework,^[1,2] but is still rarely used for the design of functional frameworks such as magnets.^[3] For 2D layered magnetic frameworks, the pillars, when introduced between the layers, determine the interlayer interactions. Thus, if the pillars consist of a paramagnetic species, this structural model rationally leads to the construction of a 3D magnetic pathway through an infinite framework, which is advantageous for creating magnets.

Herein we report a ferrimagnet with $T_C > 80$ K achieved in a unique PLF that is rationally constructed by integrating magnetic layers and π -stacked magnetic columns as the pillars. For the magnetic layers, a series of charge transfer D_2A compounds composed of a paddlewheel-type diruthenium(II, II) complex ($[\text{Ru}_2^{\text{II,II}}]$ as the donor (D)) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ as the acceptor (A)) was chosen.^[4,5] It has been demonstrated that the magnetic behavior of this complex is strongly affected by both the interlayer environments associated with the elimination of the crystallization solvents located between the layers and the stacking mode of the layers, even if magnetic ordering occurs at relatively high temperatures [T_C or T_N (Néel temperature for antiferromagnets) > 50 K] because of the presence of strong intralayer magnetic couplings.^[4a,b,e-g,o] In order for the pillars to be able to stabilize the interlayer interactions, the charge transfer system $[\text{FeCp}^*_2]\text{TCNQ}$ ($[\text{FeCp}^*_2]^+$ = decamethylferrocenium) was selected. This system was reported by Miller et al.^[6] and is known to form a π -stacked alternating column comprised of ferromagnetically coupled Coulombic sets, $[\text{FeCp}^*_2]^+$ and TCNQ^- , with $S = 1/2$. When combined with the layered D_2A , the $[\text{FeCp}^*_2]^+$ unit acts as a π -stacked pillar for the D_2A layers sandwiched between the TCNQ^- moieties, which consequently results in the construction of a π -stacked PLF with the formula $[\text{FeCp}^*_2][\{\text{Ru}_2\}_2\text{TCNQ}]$ (Figure 1).

This material was synthesized by assembling $[\text{Ru}_2^{\text{II,II}}(2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2)_4]$ ($2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2 = 2,3,5,6\text{-tetrafluorobenzoate}$) with $[\text{FeCp}^*_2]\text{TCNQ}$ in a 2:1 ratio to yield $[\text{FeCp}^*_2][\{\text{Ru}_2^{\text{II,II}}(2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2)_4\}_2\text{TCNQ}] \cdot 2\text{DCE}$ (**1**; DCE = 1,2-dichloroethane; see the Supporting Information). The compound $[\text{Ru}_2^{\text{II,II}}(2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2)_4]$ was chosen because of its high stability; given the $[\text{Ru}_2^{\text{II,II}}]$ oxidation state in this material against that of TCNQ^- , further electron transfer, which would enable the formation of TCNQ^{2-} , was not expected to occur.^[7] The infrared (IR) spectrum of

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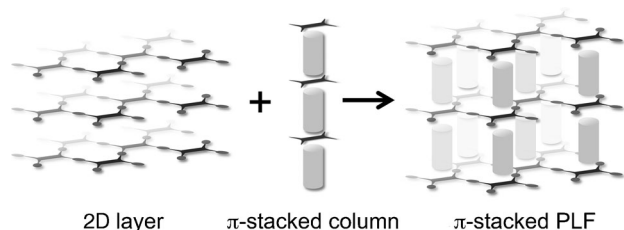


Figure 1. Schematic representation of the design of a π -stacked PLF by integration of a layered framework system and a 1D columnar system.

1 exhibited characteristic $\text{C}\equiv\text{N}$ vibrational modes attributable to the TCNQ moiety at 2161 and 2200 cm^{-1} (Supporting Information, Figure S1), indicating that as expected, the TCNQ moiety exists as $\text{TCNQ}^{\cdot-}$ in this assembly.^[4f]

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a formula unit comprising two $\{\text{Ru}_2\}$ units, one TCNQ unit, and one $[\text{FeCp}^*_2]$ molecule, each of which has an inversion center on the midpoint of the respective units/molecules ($Z = 1$; Figure 2a; for details see the Supporting Information).^[8] The four CN groups of TCNQ coordinate to the axial sites of the $\{\text{Ru}_2\}$ units, forming a typical $\text{D}_{2\text{A}}$ -type 2D fishnet framework (Figure 2b) similar to previously reported compounds.^[4a,b,e-g,j,k] The oxidation state of each unit in the $\text{D}_{2\text{A}}$ compound can be determined from the structure; $\text{Ru}-\text{O}_{\text{eq}}$ (O_{eq} = carboxylate oxygen atom) bond distances are more sensitive to the oxidation state and are generally in the range of 2.07–2.09 Å for $\{\text{Ru}_2^{\text{II,III}}\}$ and 2.01–2.03 Å for $\{\text{Ru}_2^{\text{III,III}}\}$. The average $\text{Ru}-\text{O}_{\text{eq}}$ bond lengths (Table S1) in **1** are 2.067 Å for $\{\text{Ru}(1)_2\}$ and 2.074 Å for $\{\text{Ru}(2)_2\}$; both values suggest a $\{\text{Ru}_2^{\text{II,III}}\}$ oxidation state. Meanwhile, the component bonds in TCNQ characteristically reflect its oxidation state according to Kistenmacher's relationship ($\rho = A[c/(b+d)] + B$),^[9] where b , c , and d are the respective bond distances for the 7,9-, 1,7-, and 1,2-positioned C–C sets in the TCNQ moiety (Table S2), and A (−41.667) and B (+19.833) are parameters determined by assuming a completely neutral and one-electron-reduced form of TCNQ, such as TCNQ^0 ($\rho = 0$)^[10] and RbTCNQ ($\rho = -1$)^[11] respectively. The estimated ρ value was −0.99, indicating that the TCNQ unit is a radical monoanion ($\text{TCNQ}^{\cdot-}$). Considering these charge distributions on the $\{\text{Ru}_2\}$ and TCNQ units, to form an anionic $\text{D}_{2\text{A}}$ layer (i.e., $[\text{D}_{2\text{A}}]^-$), the $[\text{FeCp}^*_2]$ molecule must adopt the monocationic form as $[\text{FeCp}^*_2]^+$. In general, for $[\text{Fe}^{\text{II}}\text{Cp}^*_2]$ and $[\text{Fe}^{\text{III}}\text{Cp}^*_2]^+$, the average $\text{C}\cdots\text{Fe}$ distances are approximately 2.05 Å and 2.10 Å, respectively, and the distances between the centroid of the C_5 pentagon ring and Fe tend to be approximately 1.65 Å and 1.70 Å, respectively.^[12] The two corresponding values for **1** were found to be 2.096 Å and 1.708 Å (Table S3), indicating that the $[\text{FeCp}^*_2]$ molecule was indeed present in the monocationic form.

The compound can thus be formally written as $[\text{FeCp}^*_2]^+ \cdot [\{\text{Ru}_2^{\text{II,III}}\}_2(\text{TCNQ})^-]$, and the $[\text{FeCp}^*_2]^+$ molecules build a π -stacked pillar connecting $\text{D}_{2\text{A}}$ layers to form a PLF with a π -stacked alternating column of $[\cdots[\text{FeCp}^*_2]^+ \cdots \text{TCNQ}^{\cdot-} \cdots]$, as observed in Miller's original compound (Figure 2c).^[6b] The inter-TCNQ distance through $[\text{FeCp}^*_2]^+$ is 10.31 Å (i.e.,

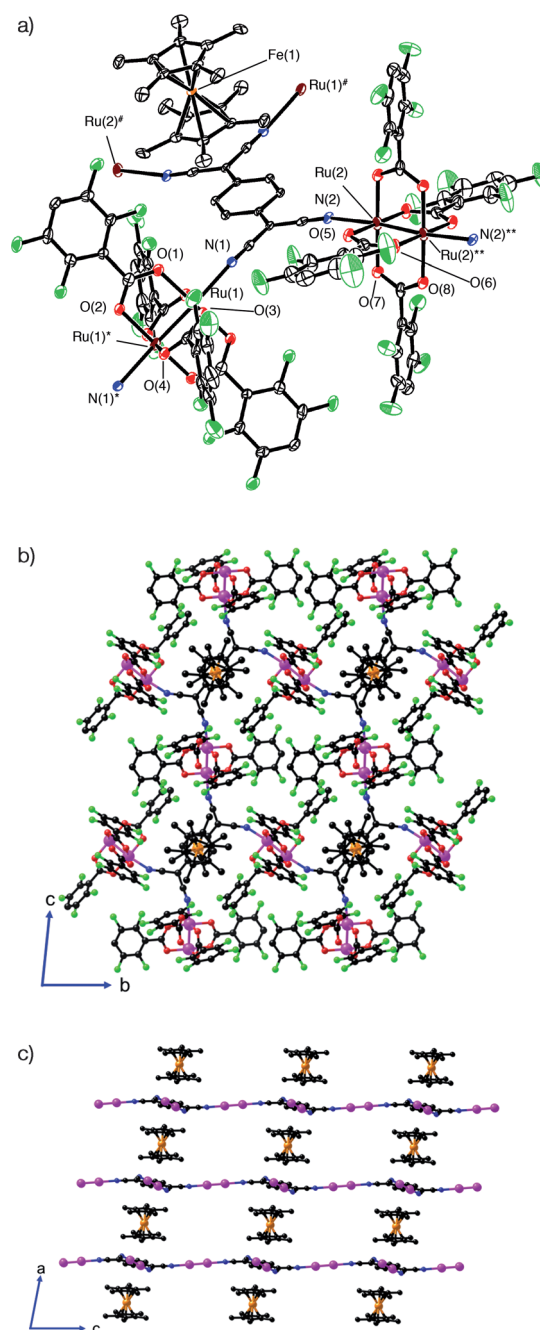


Figure 2. a–c) Structure of **1**: ORTEP representation of the formula unit (a) and packing views projected along the a axis (b) and the b axis (c). Hydrogen atoms and crystallization solvents are omitted in all of the figures for clarity, and the 2,3,5,6- $\text{F}_4\text{C}_6\text{HCO}_2^-$ ligands around the Ru centers are omitted in (c).

$d(\text{TCNQ}\cdots\text{Fe}) = 5.155$ Å), which corresponds to the inter-layer distance and is shorter than that in $[\text{FeCp}^*_2]\text{TCNQ}$ (10.840(5) Å).^[6b]

The temperature dependence of the magnetic susceptibility (χ) was measured in the temperature range 1.8–300 K by applying 1 kOe, and the obtained values for χ and the product χT are given in Figure 3a. The χT value at 300 K was 2.23 $\text{cm}^3\text{K mol}^{-1}$, which is very close to the value of 2.6 $\text{cm}^3\text{K mol}^{-1}$, which would result from the spin arrange-

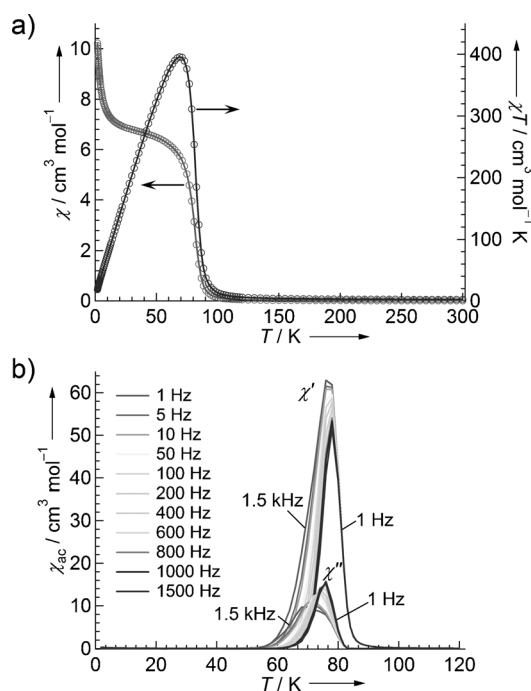


Figure 3. Temperature dependence of the a) direct current (dc) susceptibility (χ) and the χT product and b) the ac susceptibilities (χ' : in phase, χ'' : out of phase) for **1**.

ment for a ferrimagnetically ordered D_2A layer with $S_{\text{T}} = 3/2$ and isolated $[\text{FeCp}^*]^{+}$ units with $S = 1/2$ (Curie constant $C = 1.60 \text{ cm}^3 \text{K mol}^{-1}$ and Weiss constant $\theta = 87.5 \text{ K}$, determined from the χ^{-1} vs. T plot; see Figure S2). Furthermore, as the temperature decreased, the value of the χT product gradually increased; then, it steeply increased at approximately 90 K to reach a maximum of $395.8 \text{ cm}^3 \text{K mol}^{-1}$ at 69 K and subsequently rapidly decreased to $18.5 \text{ cm}^3 \text{K mol}^{-1}$ at 1.8 K. The value of χ also exhibited a steep increase at approximately 90 K, indicating the onset of magnetization, followed by a second increase at low temperatures of approximately 1.8–20 K (see below).

To gain greater insight into the long-range ordering, the alternating current (ac) susceptibilities (χ' : in phase, χ'' : out of phase) were then measured as a function of temperature (Figure 3b). The value for χ' showed a sharp peak at approximately 80 K, which was slightly dependent on the frequency. Accompanying this freezing of χ' , a χ'' peak was also observed, in which the initial rise of χ'' was observed at 82 K on cooling, giving a phase transition temperature (T_{C}).^[13] This T_{C} value is relatively high compared to those for previously reported molecule-based magnets.^[4b,d,e-g,m,13] Furthermore, the long-range ordering enabled a spontaneous magnetization, that is, ferrimagnetic ordering, because of the insertion of the intercalating paramagnetic $[\text{FeCp}^*]^{+}$ species between the layers. This behavior is interesting because similar D_2A -type layered compounds have been reported to generally exhibit antiferromagnetic long-range ordering with interlayer antiferromagnetic interactions.^[4b,e-g]

A second steep increase in the value of χ was observed at temperatures below 20 K. This anomaly of the magnetization

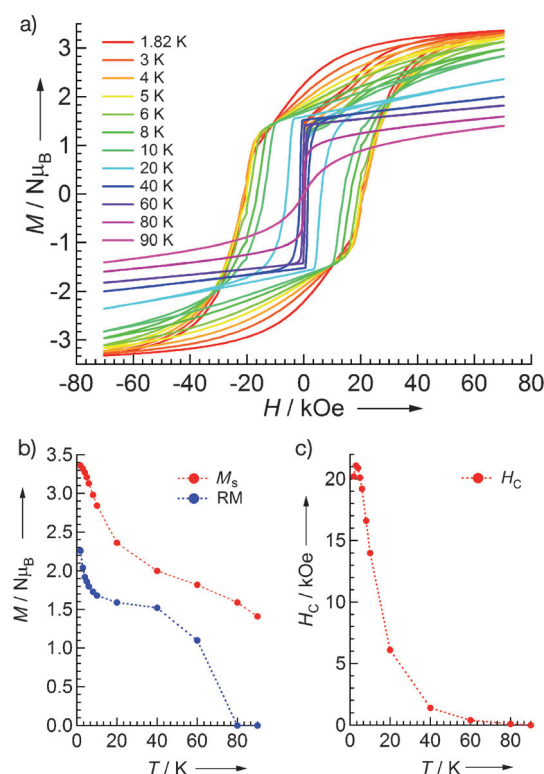


Figure 4. a) Field dependence of the magnetization of **1** measured at several temperatures in the range from 1.8–90 K. b) Temperature dependence of the saturated magnetization at 7 T (M_{s}) and the remnant magnetization (RM). c) Temperature dependence of the coercive field (H_{C}).

was characteristically seen in the field dependence of the magnetization (M – H curve), which was measured at several temperatures (Figure 4a). Hysteresis phenomena were observed at temperatures below 80 K, but their curve shapes were very different at below/above 20 K. Figure 4b illustrates the dependence of the saturated magnetization (M_{s}) at 7 T and the remnant magnetization (RM) on temperature. Both magnetization values changed substantially at the boundary around 20–30 K. At low temperatures below 20 K, the M_{s} value increased as if the total spin was increased. Along with the anomalous behavior of M_{s} , RM and the coercive field (H_{C}) also increased (Figure 4c). Considering that the spins in D_2A layers are strongly coupled and that the M – H curves for previously reported D_2A systems are very similar to those observed above 20 K, this behavior at temperatures below 20 K should be associated with the spin–orbit coupling of $[\text{FeCp}^*]^{+}$, which reduces the effective magnetic moment of $[\text{FeCp}^*]^{+}$, in particular at low temperatures.^[14]

To confirm the magnetic behavior of the $[\text{FeCp}^*]^{+}\text{TCNQ}^{-}$ column, the isostructural compound $[\text{FeCp}^*]^{+}[\text{Rh}_2^{\text{II,II}}(2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2)_4]_2\text{TCNQ}] \cdot n(\text{solv})$ (**2**) with a diamagnetic $[\text{Rh}_2^{\text{II,II}}(2,3,5,6\text{-F}_4\text{C}_6\text{HCO}_2)_4]$ unit was synthesized (see Figure S3 and the experimental section in the Supporting Information),^[8] and its magnetic properties, which are derived only from the $[\text{FeCp}^*]^{+}$ and TCNQ^{-} units, were investigated. Prior to the magnetic measurements, the

charge distribution in the $[\text{FeCp}^*_2]^+$ and TCNQ^- groups was confirmed by IR spectroscopy (Figure S1), and the presence of TCNQ^- species was indicated. At 300 K, a χT product of $1.207 \text{ cm}^3 \text{ K mol}^{-1}$ was measured, which agrees well with the presence of two isolated $S = 1/2$ spins. Upon cooling, the χT value remained nearly constant down to 76 K and then decreased to $0.676 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K, which is most likely due to the orbital contribution of $[\text{FeCp}^*_2]^+$ (Figure S4).^[14] This behavior of **2** is very different from the ferromagnetic behavior observed for the original $[\text{FeCp}^*_2]\text{TCNQ}$ compound,^[6a] but is similar to that reported for several other compounds and indicates that the magnetic interaction between the $[\text{FeCp}^*_2]^+$ and TCNQ^- units is weak.^[15] This result suggests that the orbital contribution of $[\text{FeCp}^*_2]^+$ could still be active even in the assembled system of **1**. It should be noted that the $[\text{FeCp}^*_2]^+$ spin should be ferromagnetically aligned through the $[\text{FeCp}^*_2]\text{TCNQ}$ column in **1**, as well as in the original compound,^[6,16,17] although its coupling with the TCNQ^- spin was observed to be weak in **2**, because only the ferromagnetic spin arrangement in the $[\text{FeCp}^*_2]\text{TCNQ}$ column enables an increase in S_T by the reduction of the magnetic moment of $[\text{FeCp}^*_2]^+$ (case **A** in Figure 5).

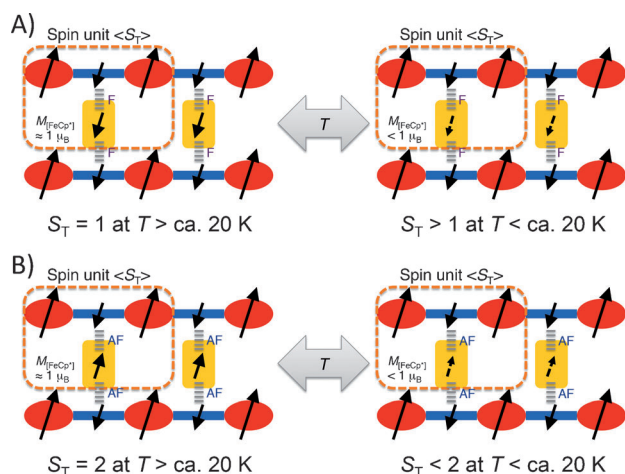


Figure 5. The variation of the magnetization is due to spin-orbit coupling with $[\text{FeCp}^*_2]^+$ (yellow box). In case **A**, with a ferromagnetic spin arrangement in the $[\text{FeCp}^*_2]\text{TCNQ}$ column, the spin unit $S_T = 1$ for the formula changes as if it increased to $S_T > 1$ when the $[\text{FeCp}^*_2]^+$ spin was apparently reduced by the spin-orbit coupling, whereas in case **B**, with an antiferromagnetic spin arrangement in the $[\text{FeCp}^*_2]\text{TCNQ}$ column, the spin unit $S_T = 2$ for the formula changes as if it was reduced to $S_T < 2$.

Finally, tuning of the T_C value using an external stimulus was investigated. Hydrostatic pressures up to 12.5 kbar were applied to **1** using a piston-cylinder-type cell fabricated from a Cu–Be alloy with a Pb probe.^[18,19] As the pressure increased, the onset of magnetization, which indicates T_C , shifted to higher temperatures (Figure 6). Notably, the relationship between the T_C value and the pressure was found to be linear (Figure 6, inset). At the highest applied pressure of 12.5 kbar, a T_C value of 107 K was recorded.

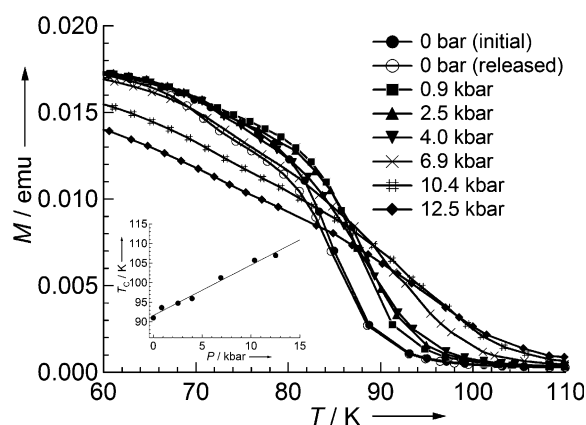


Figure 6. Temperature dependence of the magnetization of **1** measured at several applied pressures up to 12.5 kbar. Inset: Variation of T_C as a function of the applied pressure.

In summary, a π -stacked PLF was rationally designed and constructed, providing a magnet that is based on two combined low-dimensional parts, namely a covalently bonded D_2A layered framework and a charge transfer $[\text{FeCp}^*_2]\text{TCNQ}$ stacked system, with preservation of the respective characteristics. Interlayer interactions were confirmed to be crucial in determining the ordered state of the two-dimensional D_2A material whereas many such materials were previously revealed to be antiferromagnets or related magnets.^[4b,e–g] Importantly, the insertion of paramagnetic $[\text{FeCp}^*_2]^+$ units between the D_2A layers succeeded in aligning the spins to yield a ferrimagnetic ordered state in the bulk. Consequently, this framework design led to the fabrication of a material with a relatively high phase transition temperature that increased linearly with the applied pressure.

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