The discovery of conductive and magnetic two-dimensional (2D) materials is critical for the development of next generation spintronics devices. Coordination chemistry in particular represents a highly versatile, though underutilized, route toward the synthesis of such materials with designer lattices. Here, we report the synthesis of a conductive, layered 2D metal–organic kagome lattice, \( \text{Mn}_3(\text{C}_6\text{S}_6) \), using mild solution-phase chemistry. Strong geometric spin frustration in this system mediates spin freezing at low temperatures, which results in glassy magnetic behavior consistent with a geometrically frustrated (topological) spin glass. Notably, the material exhibits a large exchange bias of 1625 Oe, providing the first example of exchange bias in a coordination solid or a topological spin glass. More generally, these results demonstrate the potential utility of geometrically frustrated lattices in the design of new nanoscale spintronic materials.
Exchange Bias in a Layered Metal–Organic Topological Spin Glass

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The discovery of conductive and magnetic two-dimensional (2D) materials is critical for the development of next generation spintronics devices. Coordination chemistry in particular represents a highly versatile, though underutilized, route toward the synthesis of such materials with designer lattices. Here, we report the synthesis of a conductive, layered 2D metal–organic kagome lattice, $\text{Mn}_3(\text{C}_6\text{S}_6)$, using mild solution-phase chemistry. Strong geometric spin frustration in this system mediates spin freezing at low temperatures, which results in glassy magnetic behavior consistent with a geometrically frustrated (topological) spin glass. Notably, the material exhibits a large exchange bias of 1625 Oe, providing the first example of exchange bias in a coordination solid or a topological spin glass. More generally, these results demonstrate the potential utility of geometrically frustrated lattices in the design of new nanoscale spintronic materials.

The nascent field of two-dimensional (2D) magnetism has outlined a path toward nanoscale spintronics devices that leverage magnetic degrees of freedom\textsuperscript{1}. Along these lines, materials that exhibit exchange bias, characterized by a horizontal shift in the origin of the magnetic hysteresis loop, are of particular interest. Exchange bias is widely employed in spin valves used in hard disk read heads\textsuperscript{2}, is used to stabilize magnetic storage media\textsuperscript{3}, and shows promise for more exotic spintronics applications, such as electrical switching of magnetic logic devices\textsuperscript{4}. While exchange bias has been extensively demonstrated in antiferromagnetic/ferromagnetic thin film interfaces\textsuperscript{5} and nanoparticle systems\textsuperscript{6}, this property has yet to be demonstrated in 2D materials suitable for the development of nanoscale spintronics devices. Although the microscopic origin of exchange bias is yet unresolved\textsuperscript{6}, recent studies underscore the critical role that spin frustration may play—most explicitly demonstrated by the observation of exchange bias not only at ferromagnetic/spin glass interfaces\textsuperscript{7}, but also in single phase, amorphous spin glasses\textsuperscript{8}. In such systems, disorder-
induced spin frustration engenders glassy behavior, which has been linked to the observation of exchange bias and the relaxation of the bias field upon cycling.

We hypothesized that spin frustration arising not from disorder but from geometrically frustrated lattices may also result in exchange bias. Such lattices, comprised of spins arranged in a triangular pattern, engender frustration when antiferromagnetic coupling is dominant, since three spins at the corners of a triangle cannot all align in an antiparallel fashion. As the temperature is lowered, correlated spins in such lattices may “freeze” in certain circumstances, forming a disordered magnetic phase termed a topological spin glass. More generally, the design of 2D frustrated magnetic lattices is of inherent interest for studies at the nanoscale, as these lattices are implicated in a variety of exotic correlated phenomena, such as quantum spin liquid behavior, superconductivity, and spin neumaticity. Saliently, a number of layered metal–organic coordination solids with kagome-like frustrated 2D lattices have recently been reported, wherein π–d conjugation gives rise to materials exhibiting varied charge transport behavior, ranging from semiconductors to superconductors. However, experimental realization of the diverse magnetic behavior predicted in these materials remains limited, likely due to the synthetic difficulty of achieving the requisite square planar coordination geometry with transition metals of interest.

Here, we report the layered 2D coordination solid Mn₃(C₆S₆), which consists of high-spin Mn²⁺ ions templated into a kagome lattice by benzenehexathiol. This material displays conductivity values reaching ~1.50 S/cm at room temperature, while magnetic characterization reveals a high degree of spin frustration, with antiferromagnetic coupling at room temperature and a spin canted antiferromagnetic glassy state at low temperatures. Remarkably, Mn₃(C₆S₆) also displays a large exchange bias upon magnetic field annealing. The dynamic magnetic
properties of this solid are consistent with geometric, rather than disorder-induced, spin
frustration, indicating Mn₃(C₆S₆) is a topological spin glass. These results highlight a potentially
powerful strategy for the design of novel exchange bias systems that relies on crystalline
frustrated lattices rather than serendipitously disordered interfaces. Beyond potential applications
in biased spintronics devices, Mn₃(C₆S₆) stands as a tunable platform for the fundamental study
of frustrated magnetism at the nanoscale.

Synthesis and Structure of Mn₃(C₆S₆)

The material Mn₃(C₆S₆) was synthesized at the liquid-liquid interface of an aqueous solution of
Mn(CH₃CO₂)₂·4H₂O and a dichloromethane solution of benzenehexathiol under an atmosphere
of 95% N₂ and 5% H₂. Slow addition of these solutions to pure layers of their respective solvents
produced a yellow-gold film with an iridescent sheen (Supplementary Fig. 1). Scanning electron
microscopy characterization of this film revealed a morphology similar to the previously
reported Cu₃(C₆S₆) phase, wherein the side of the film facing the organic phase is smooth and the
opposite side is composed of smaller crystallites (Supplementary Fig. 2)¹⁸.

Synchrotron powder X-ray diffraction data for Mn₃(C₆S₆) revealed a crystalline material with
a structure similar to that of Cu₃(C₆S₆) (Fig. 1)¹⁸. Simulated powder X-ray diffraction patterns for
eclipsed and staggered stacking models of Mn₃(C₆S₆) (Supplementary Fig. 3) suggest that the
structure is closer to one with an eclipsed conformation. Broadening in the peaks corresponding
to c-axis reflections is attributed to the inherent anisotropy of the flake-like crystals, although
minor stacking disorder may contribute as well. Peak indexing revealed a hexagonal lattice with
an in-plane lattice parameter of 8.62 Å and an estimated interlayer distance of 3.77 Å. Inductively coupled plasma-mass spectrometry analysis of the crystalline solid afforded an
empirical formula of Mn₀.₉₉:S₁, consistent with the expected formula of Mn₀.₅:S₁. The infrared
spectrum of $\text{Mn}_3(\text{C}_6\text{S}_6)$ (Supplementary Fig. 4) features C–S stretches consistent with those reported in $\text{Cu}_3(\text{C}_6\text{S}_6)^{15}$, establishing the ligand as $\text{C}_6\text{S}_6^{6-}$, while the absence of C–H and O–H stretching frequencies from 2800 to 3500 cm$^{-1}$ indicated the absence of coordinated solvent, as expected given the calculated interlayer distance. The X-ray photoelectron spectrum of $\text{Mn}_3(\text{C}_6\text{S}_6)$ could be fit assuming the presence of only one Mn, S, and C species (Supplementary Fig. 5), further supporting the conclusion that the manganese and ligand are valence pure$^{19}$. In the Mn K-edge X-ray absorption near edge structure (XANES) spectrum of $\text{Mn}_3(\text{C}_6\text{S}_6)$, the rising edge energy of $\sim$6548 eV coincides with that of a MnS standard, while a small pre-edge feature is consistent with local inversion symmetry, as would be expected for the proposed square planar geometry (Supplementary Fig. 6). Together, the diffraction and spectroscopic data are consistent with an assignment of $\text{Mn}^{\text{II}}_3(\text{C}_6\text{S}_6^{6-})$, in which the manganese ions form a 2D kagome lattice.

**Conductivity and Electronic Structure**

An average room temperature conductivity value of $\sigma = 0.39$ S/cm was determined from van der Pauw conductivity measurements on thin film (100–200 nm thick) samples of $\text{Mn}_3(\text{C}_6\text{S}_6)$, with a champion device exhibiting a value of 1.48 S/cm. The variance in conductivity values (Supplementary Table 1) is similar to that characterized in other metal–organic materials$^{20}$ and likely stems from differences in interparticle contacts and film continuity across the device. Variable-temperature conductivity measurements were performed on a pressed pellet of $\text{Mn}_3(\text{C}_6\text{S}_6)$ using a 2-point screw cell with copper contacts. The data were adequately fit using an Efros-Shklovskii variable-range hopping model (Supplementary Figs. 7 and 8), as is typical for charge transport in low-dimensional and polycrystalline materials limited by interparticle contacts$^{21,22}$. Thermopower measurements on the thin film samples afforded Seebeck coefficients as high as 169 $\mu$V·K$^{-1}$ (Supplementary Table 1), suggesting that $\text{Mn}_3(\text{C}_6\text{S}_6)$ is a p-type
semiconductor. Indeed, the UV–Vis–NIR spectrum of Mn$_3$(C$_6$S$_6$) displays a monotonic increase in absorption in the near-IR region that is indicative of thermally-activated charge carriers (Supplementary Fig. 9) $^{22-25}$. Notably, the corresponding power factor of 4.08 $\mu$W/mK$^2$ surpasses values obtained for structurally similar metal–organic materials$^{18,26}$. Density functional theory calculations on bulk crystals with spin canted configurations, including spin-orbit coupling and van der Waals corrections, are consistent with semiconducting behavior, yielding calculated direct gaps on the order of $\sim$1 eV (Fig. 2, left). Notably, the valence band contains significant Mn, S, and C orbital character, highlighting the importance of covalency in enabling electronic coupling within the material (Fig. 2, right).

**Magnetic Properties**

Strong antiferromagnetic interactions in Mn$_3$(C$_6$S$_6$) at room temperature are evidenced by a magnetic susceptibility-temperature product of $\chi_m T = 6.94$ emu·K/mol, far below the 13.13 emu·K/mol expected for three isolated high-spin Mn$^{II}$ centers (Supplementary Fig. 11). This is corroborated by a Curie-Weiss analysis, which gives $\Theta = -253$ K, while the calculated Curie constant of 13.03 emu·K/mol is consistent with three $S = 5/2$ Mn$^{II}$ ions per formula unit (Supplementary Fig. 12). In the $\chi_m$ versus $T$ data, a peak at $\sim$12 K and the divergence between field-cooled (FC) and zero field-cooled (ZFC) traces (Fig. 3a) are indicative of the onset of a spin freezing transition, $T_F$. The disparity between $|\Theta|$ and this transition temperature is attributed to geometric frustration induced by the kagome lattice, which is well known to give lower ordering temperatures than those expected from the strength of magnetic interactions. The Ramirez ratio, $f = |\Theta|/T_F$, is commonly used to quantify spin frustration, and the value of $f \sim 20$ obtained for Mn$_3$(C$_6$S$_6$) is indicative of a high degree of frustration$^{11}$. Moreover, ac magnetic
susceptibility data reveal a frequency dependence of $T_r$, with a Mydosh parameter of $\sim 0.015$ (Fig. 3b–c), consistent with spin glass behavior associated with frustrated magnets\textsuperscript{27}.

Spin glasses are characterized by an energy landscape featuring numerous, nearly degenerate states that arise from spin frustration. This landscape can be probed by monitoring changes in magnetization with changing temperature, applied magnetic field, and time, perhaps most uniquely through the demonstration of a thermal memory\textsuperscript{27,28}. To examine this memory effect, a sample of Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}) was cooled under zero field from 30 K and held for 10 min at 10, 8, and 6 K temperature points (Fig. 4a). At each temperature pause, the material will traverse the available energy landscape to reach an associated metastable state. After these temperature pauses, ZFC magnetic susceptibility data were collected under 100 Oe, revealing thermal memory at the set wait points, as evidenced by “memory dips” in the measured susceptibility (Fig. 4b, red trace). A partial rejuvenation of the susceptibility (an increase after a dip) is observed upon warming as the system gains the requisite thermal energy to re-equilibrate within the energy landscape. In this context, bifurcation of the FC and ZFC dc susceptibility data (Fig. 3a) is consistent with a spin glass state, for which application of a magnetic field enables access to higher moment, metastable states.

The complex energy landscape of a spin glass engenders nontrivial magnetic relaxation processes. To investigate the glassy relaxation dynamics of Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}), thermoremanent magnetization experiments were performed following the protocol outlined in Fig. 4c. The material was first cooled from 30 to 2 K under a 100-Oe field and held for a given waiting time ($t_w$); the field was then zeroed and the change in magnetization was monitored. As seen in the decay curves in Fig. 4d, longer $t_w$ values are associated with higher magnetization values, characteristic of a glassy magnetic system\textsuperscript{27,28}. Fits of the magnetization decay curves using a
stretched exponential function yielded τ values on the order of 10^2 years (Supplementary Table 2). Electronic structure calculations performed on five possible spin conformations in Mn₃(C₆S₆) (Supplementary Table 3) indicate that coplanar antiferromagnetic spin arrangements are lowest in energy. The resulting small energy differences between the various antiferromagnetic configurations are also likely critical to the observation of glassy behavior. Variable-field magnetization data collected at 2 K after cooling under zero field revealed an open hysteresis loop with a coercive field, H_c, of 2000 Oe that does not saturate as high as 7 T, which could indicate spin canting similar to that observed in S = 3/2 Heisenberg kagome lattices (Supplementary Fig. 13)^29.

Variable-field magnetization data collected upon cooling under ±1 T revealed hysteresis with a pronounced lateral origin shift from zero to ±1625 Oe, accompanied by an increase in H_c by 395 Oe (Fig. 5a–b), consistent with the exchange bias effect^6,7,27. The stability of the exchange bias was examined by cooling Mn₃(C₆S₆) under 1 T, ramping the field to 0 T, and then collecting hysteresis data after a 60-min waiting period (Fig. 5c). The corresponding loop is essentially unchanged from that characterized immediately after cooling under 1 T, indicating that the exchange bias is nonvolatile. Several successive hysteresis loops were also collected after cooling the sample under 1 T. Both H_c and the exchange bias field, H_e, trend toward a constant value with increasing cycle number (Supplementary Fig. 14), consistent with the magnetic training effect in exchange biased systems. Hysteresis data collected after cooling Mn₃(C₆S₆) under different fields revealed that H_c achieves a maximum at 1 T (Supplementary Fig. 15). As such, the exchange bias likely cannot be attributed to the small crystallite morphology of Mn₃(C₆S₆), given that single-phase, superparamagnetic particles displaying exchange bias do so even under large applied fields, owing to the presence of a well-behaved magnetic core coupled
with surface states exhibiting glassy dynamics\textsuperscript{6,7,30}. An exchange bias is also observed following application of a 1 T field for a 1-h induction period after zero field cooling, indicating that \textit{isothermal} magnetic switching is possible in this system (Fig. 5d). Importantly, this observation is entirely at odds with the existence of a minor loop phenomenon (see discussion in Supplementary Information). Further, this isothermal switching is not observed in antiferromagnetic/ferromagnetic exchange bias systems, suggesting a unique mechanism is responsible for the behavior observed here.

Glassy magnetic behavior typically originates from significant structural disorder; however, the myriad structural data for Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}) establish the homogenous, crystalline nature of the 2D plane. To elucidate whether the spin glass state mediating exchange bias originates from small amounts of local/stacking disorder or is a consequence of system geometric frustration, we employed a suite of magnetic characterization methods capable of probing the unique history-dependent dynamics inherent to the energy landscape of a geometrically frustrated glass\textsuperscript{31}. First, in disordered spin glasses, a distinct peak associated with $t_w$ is typically observed in the time-dependent derivative of the thermoremanent magnetization, which is caused by a distribution of superparamagnetic clusters with individual relaxation times; those with relaxation times on the order of $t_w$ magnetize during aging and subsequently relax on that same timescale\textsuperscript{27,28}. In contrast, $dM/dt$ versus $t$ curves derived from the data in Fig. 4d overlay, suggesting that the characteristic relaxation time of the glass is essentially unaffected by the aging history of the material (Fig. 6a and Supplementary Table 2). In other words, the spin-reversal barriers within the energy landscape of Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}) are significantly less dynamic in response to the time-dependent history of the material compared to structurally disordered glasses. Magnetization relaxation in Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}) was also examined following the temperature perturbation protocol illustrated in Fig. 6b, wherein after cooling from 30 to 2 K under 100 Oe, separate waiting periods of 1500 and 300
s are punctuated by a 60 s period at 4 K. The thermoremanent magnetization curve collected after this temperature cycling sequence (Fig. 6c, red trace) exhibits a larger frozen moment than that for a magnetization decay curve collected after a $t_w$ of 300 s without a temperature perturbation (Fig. 6c, purple trace). A similar phenomenon has been observed for the topological spin glass $(H_2O)Fe_3(SO_4)_2(OH)_6$ and is distinct from the behavior of disordered glasses, where temperature cycling resets aging. This result for $Mn_3(C_6S_6)$ is further corroborated by the incomplete rejuvenation of the memory dip curve to the baseline curve: the energy landscape of a geometrically frustrated glass is less sensitive to temperature perturbation (Fig. 4b). Together, these findings suggest that the energy landscape of $Mn_3(C_6S_6)$ is significantly less dynamic than that of a disordered spin glass, but rather is consistent with a topological spin glass.

The magnetic glass transition is a second-order phenomenon, and therefore a higher-order magnetic susceptibility term is needed to interrogate the phase transition. The nonlinear susceptibility, $\chi_3$, of $Mn_3(C_6S_6)$ was extracted from a series of magnetization isotherms around $T_F$. In disordered spin glasses, $\chi_3(T) \propto (T-T_g)^\gamma$ ($2 < \gamma < 3$) for temperatures approaching $T_F$. In the case of $Mn_3(C_6S_6)$, $\chi_3$ versus $T$ is both nonzero as high as 50 K and diverges to a far lesser degree than is observed in canonical spin glasses, such that the data could not be fit to the aforementioned power law (Fig. 6d). This behavior suggests a build-up of correlated spin dynamics well above the glass transition, as predicted by topological spin glass theory and previously observed in hydronium iron jarosite. The divergence of the FC and ZFC traces (Fig. 3a) far above the glass transition temperature corroborates this observation, as it suggests that temperature and field are dynamically modifying correlated, unfrozen spins. Together, these experiments demonstrate that the glassy dynamics of $Mn_3(C_6S_6)$ likely originate from geometric frustration, rather than from structural disorder, doping effects, or long-range magnetic interactions. This finding is consistent with previous theoretical and experimental studies, which
indicated that significant disorder is necessary to shift the glassy dynamical behavior of a frustrated lattice into the disordered regime\textsuperscript{33,35-37}.

Given that structural and magnetic data do not support disorder in Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}), we propose an alternative explanation for the exchange bias that invokes an interplay of antisymmetric exchange and magnetic field-mediated chiral induction of the spin texture\textsuperscript{38,39}. Field-dependent chiral magnetic order has been theoretically proposed\textsuperscript{40} and experimentally verified\textsuperscript{29} in Heisenberg kagome antiferromagnets, in particular in potassium iron jarosite, a spin congener of Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}). Importantly, theoretical studies suggest that the chiral order observed in these magnetically ordered systems is retained locally in topological spin glasses\textsuperscript{9,10}. These local, correlated spin objects, termed topological domain wall defects or “spin folds”, have likewise been predicted to select specific chirality based on field-dependent anisotropic exchange interactions\textsuperscript{9,10,40}. We posit that the application of a magnetic field polarizes and selects the chirality of the spin folds, while the strength of the field determines the number of correlated spins within each fold and the anisotropy field. Only a fraction of the spin folds is repolarized upon a reverse field sweep, resulting in the shifted hysteresis loop. This explanation has similarities to what has been proposed in canonical spin glasses\textsuperscript{39}, but with a key distinction. In the case of canonical spin glasses, the first field-intercept of the hysteresis loop is independent of the annealing field, which has been interpreted as arising from the introduction of a rigid chiral spin texture in the material, even in the presence of a small magnetic field. In Mn\textsubscript{3}(C\textsubscript{6}S\textsubscript{6}), this first intercept gradually grows until it reaches a set value, instead suggesting that chiral induction is incomplete until a critical field is applied (Supplementary Fig. 17). A complex chiral equilibrium such as this has been previously invoked to explain the unusual relaxation behavior in topological spin glasses\textsuperscript{32}. A comparison of hysteresis loops collected after zero field cooling
and field annealing for two different wait times (30 and 300 s) highlights this point further (Supplementary Fig. 18). While the initial magnetization of the hysteresis loop is unaffected, indicating the absence of aging and polarized domain growth, the exchange bias increases by 14% with the longer induction period. In this context, the bias field may be seen as a probe of the net chirality of the system.

**Outlook**

The foregoing results demonstrate that bulk topological spin freezing alone can engender exchange bias. Initial investigations of several other site-ordered, geometrically frustrated spin glasses suggest that this design principle holds generally (Supplementary Fig. 19). Further, these results reveal a new direction in the study of frustrated magnetism, where spin folds in topologically frustrated glasses may be tuned and observed through exchange bias experiments. Modification of the magnetic and electronic properties of Mn$_3$(C$_6$S$_6$) through isoreticular chemistry and/or doping stands as a promising avenue toward accessing materials exhibiting a large exchange bias at even higher temperatures. More generally, engineering more strongly anisotropic topological spin glasses will likely result in weaker frustration, technologically-relevant freezing temperatures, and larger exchange bias. Finally, spin glass theory underpins a range of technologically important fields, from neural networks to quantum annealing, highlighting the importance of further study of the predicted non-Abelian dynamics in low-dimensional topological spin glasses, such as Mn$_3$C$_6$S$_6$, at the nanoscale.
Methods

General Information

All manipulations of the reported materials were performed inside either the Ar atmosphere of an MBRAUN glovebox or a 95/5% N₂/H₂ atmosphere in a custom VAC Atmospheres glovebox. Infrared spectra were collected on a Perkin Elmer Avatar Spectrum 400 FTIR spectrometer under an atmosphere of N₂. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out at the Microanalytical Laboratory of the University of California using a Perkin Elmer Optima 7000 DV ICP-OES. Samples were digested in 70% nitric acid in water. Benzenehexathiol was synthesized according to a previously published procedure. Dichloromethane was dried using a commercial solvent purification system designed by JC Meyer Solvent Systems. Water obtained from a Milli-Q system was sparged with Ar for 2 h before use. All other reagents were obtained from commercial vendors and used without further purification.

Synthesis of Mn₃(C₆S₆)

In an atmosphere of 95% N₂ and 5% H₂, degassed dichloromethane (40 mL) and degassed water (40 mL) were added to a 100 mL reaction vessel. Separately, benzenehexathiol (4.5 mg, 0.017 mmol) was suspended in dichloromethane (4 mL) and added to the bottom of the dichloromethane layer over a period of 20 min. A solution of Mn(CH₃CO₂)₂ (25 mg, 0.14 mmol) in water (4 mL) was then added to the water layer over 20 min. After 1 h, a translucent gold film had formed. Longer reaction times resulted in thicker films. After decanting the solvent, Mn₃(C₆S₆) was washed with water, dichloromethane, and methanol before drying under reduced pressure at 50 °C for one day.
Powder X-Ray Diffraction

Under an atmosphere of 95% N$_2$ and 5% H$_2$, a film of Mn$_3$(C$_6$S$_6$) was liberated from the organic/water interface, gently ground to a powder, and packed into borosilicate glass capillaries. High resolution X-ray powder diffraction data were collected at the Advanced Photon Source (APS) at Argonne National Laboratory at 298 K, using a wavelength of 0.45241(4) Å. A peak search, followed by indexing via the Single Value Decomposition method$^{43}$, was executed in TOPAS-Academic$^{44}$, allowing for approximate unit cell determination. Materials Studio was employed to model candidate structures.

UV-Visible-NIR Spectroscopy

A sample of Mn$_3$(C$_6$S$_6$) was ground with the non-absorbing matrix Ba(SO$_4$) and held in a Praying Mantis air-free diffuse reflectance cell. A CARY 5000 spectrophotometer interfaced with Varian Win UV software was used to collected diffuse reflectance spectra. The Kubelka–Munk function $F(R) = ((1-R)^2)/2R$ was applied to the raw diffuse reflectance spectrum to convert to pseudo-absorbance equivalent data.

IR Spectroscopy

Fourier transform infrared (FTIR) spectra were collected on a Perkin Elmer Avatar Spectrum 400 FTIR spectrometer. Attenuated total reflectance FTIR spectra were measured with a Pike attenuated total reflectance accessory. To prepare the transmission FTIR sample, Mn$_3$(C$_6$S$_6$) was ground with Nujol and sandwiched between 2 polished NaCl optical plates. To prevent sample oxidation, a glovebag was sealed onto the sample stage and purged with N$_2$ for 1 h before introducing the sample.
Conductivity Measurements

To produce thin films of Mn₃(C₆S₆) for conductivity measurements, the same synthetic protocol was carried out as described above, with a reaction time of 30 min, with the addition of a glass support 0.5 cm below the organic/aqueous interface. After film formation, the organic layer was slowly syringed from the reaction vessel, resulting in deposition of the film onto the glass substrate. For variable temperature pressed pellet measurements, a 370 µm-thick pellet of Mn₃(C₆S₆) was pressed in a custom two-electrode screw cell with copper contacts polished to a mirror finish. The screw cell was sealed using Torr Seal® low vapor pressure epoxy to prevent sample oxidation. Variable temperature conductivity measurements were performed in the sample chamber of a Quantum Design MPMS2 SQUID magnetometer. The screw cell was affixed to a modified sample rod containing two 26 AWG silver coated copper cables sealed at the top of the rod with an air tight Swagelok fitting and a Torr Seal® low vapor pressure epoxy and lowered into the sample chamber. I-V profiles (±1 V) at different temperatures were collected using a Bio-Logic SP200 potentiostat. The temperature dependence of the conductivity was best fit to the Efros-Shklovskii variable-range hopping equation

\[ \sigma = \sigma_0 e^{-T_0/T} \]

where \( \sigma \) is the conductivity, \( \sigma_0 \) is a pre-exponential factor, and \( T_0 \) is the characteristic temperature. For room temperature thin film measurements, the sheet resistance of each film was measured using a home-built probe station with Keithley 2400 Sourcemeters in a four-wire van-der-Pauw configuration. Colloidal silver was used to create electrical contact pads on each film. Ohmic contacts were confirmed before all measurements. For the two measured films, three measurements were performed for each continuous domain (determined by visual inspection), and averaged, and at least three domains were measured for each film. Film thickness was
measured by scratching the film and measuring the step height with a Veeco Dektak 150 profilometer. Electrical conductivity was extracted from the sheet resistance and thickness measurements. The Seebeck coefficient (thermopower) was measured using a homemade probe setup. Two Peltier devices (Ferrotec) were placed ~4 mm apart and a single current was passed through them in opposite polarities, causing one device to heat and the other to cool approximately the same amount relative to room temperature. The sample was placed across these two devices such that a thermal gradient was established (thermal paste from Wakefield Thermal S3 Solutions was used to ensure thermal contact), and the resulting open circuit voltage was measured using an Agilent 34401 multimeter. The temperature gradient was measured using two T-type thermocouples mounted in micromanipulators. The magnitude of the temperature gradient is directly related to the amount of current driven through the Peltier devices. Typically, five different gradients were established (allowed to equilibrate for 200 s between temperature changes), with ten voltage measurements taken and averaged at each $\Delta T$. All samples exhibited linear variation of open circuit voltage with $\Delta T$; this trend was used to extract Seebeck coefficient values. Data for both electrical conductivity and Seebeck coefficients were acquired using homemade Labview programs. For each measurement, at least three different samples were measured and averaged, with error bars representing standard error. Ohmic contacts were confirmed before measurements.

**X-ray photoelectron spectroscopy**

Data were collected using a Perkin Elmer PHI 5600 monochromatized XPS instrument with a Mg anode. To prevent oxygen contamination and reactivity, sample preparation and mounting were performed in an argon glovebox. The sample was affixed to a silicon wafer using double sided carbon tape. After mounting the wafer on the stage, the sample was sealed in an airtight jar
under argon. To load into the XPS, a glovebag containing the jar was sealed onto the loading chamber and subsequently purged with a high flow of argon for one hour, after which the sample was loaded into the chamber under argon. Samples were calibrated using the aromatic carbon peak as a standard. For proper peak fitting, a Shirley background was applied to regions of interest and subtracted after peak fitting. All data processing and peak fitting was performed using CasaXPS.

**Magnetic Measurements**

In an Ar filled glovebox, 18.5 mg of Mn₃(C₆S₆) was added to a 5 mm inner diameter (7 mm outer diameter) quartz tube containing a raised quartz platform, along with an equal volume of solid eicosane. The tube was fitted with Teflon sealable adapter, evacuated on a Schlenk line, and the eicosane was melted in a 40 °C water bath until a homogenous mixture of sample and eicosane was observed. This mixture prevents particle torqueing and ensures good thermal contact between sample and cryostat. The tube was then flame-sealed under static vacuum. A Quantum Design MPMS2 SQUID magnetometer equipped with a reciprocating sample option was used to perform direct current and alternating current magnetic susceptibility measurements. Ac susceptibility data were collected using a 4-Oe switching field. Variable-field magnetization measurements were performed using a sweep rate of 3 mT/s. Diamagnetic corrections of $\chi_D = -0.000168$ emu/mol (Mn₃(C₆S₆)) and $\chi_D = -0.00024306$ emu/mol (eicosane) were applied to all data. Further discussion of experimental details is provided in the Supplementary Information.

**Scanning Electron Microscopy**

Images were collected using a Hitachi S-5000 microscope operating at 30 kV. To prepare the sample displaying the bottom face of the film, a silicon wafer was lowered onto the upper surface of a freshly prepared film suspended at the aqueous/organic interface. The sample
displaying the top face of the film was prepared similarly to those used in film conductivity measurements. Samples were sputtered with gold prior to data collection to minimize potential sample charging.

**Manganese K-edge X-ray Absorption Spectroscopy**

Data were collected at the Advanced Light Source bending magnet microprobe beamline 10.3.2 (2.1–17 keV) with the storage ring operating under top-off conditions at 500 mA and 1.9 GeV.\(^{46}\) Mn\(_3\)(C\(_6\)S\(_6\)) and MnS samples were individually mounted onto Kapton tape in an Ar-filled glovebox, sealed in multiple hermetic bags, transferred to the ALS, and measured in fluorescence mode by continuously scanning the Si(111) monochromator (Quick X-ray absorption spectroscopy mode).\(^{47}\) Fluorescence emission counts were recorded with a seven-element Ge solid-state detector (Canberra) and XIA electronics. All spectra were collected from 100 eV below and up to 300 eV above the edge and calibrated using a vanadium foil, with the first derivative set at 5465.1 eV. All data were processed using LabVIEW custom software available at the beamline and further processed with Athena.\(^{48}\)

**Computational Methods**

First-principles ionic and electronic structure calculations were performed using density functional theory with a plane-wave basis and projector augmented wave (PAW) potentials as implemented by the Vienna *ab-initio* simulation package (VASP).\(^{50,51}\) All calculations are performed in the generalized gradient approximation as implemented by Perdew, Burke and Ernzerhof (PBE),\(^{52}\) with the addition of a Hubbard U term (GGA+U) to account for on-site localization on the Mn ions, using U = 4.0 eV. A plane-wave energy cut-off of 500 eV was used with a 10 × 10 × 1 Gamma-centered k-point mesh. A 20 Å vacuum insertion was used to prevent interactions between monolayers. Non-collinear spin polarized ionic relaxations, band structure,
and density of states calculations were performed for all magnetic conformations considered, with spin-orbit coupling included. All forces were converged to < 0.001 eV/Å in the structural relaxations. For monolayer calculations, a 20 Å vacuum layer was inserted to prevent interactions between adjacent layers. In the calculated bulk crystal structure, individual layers were directly aligned along the c-axis and Grimme-D3 corrections were included to account for interlayer dispersion forces\textsuperscript{53}. All forces were converged to < 0.001 eV/Å in the structural relaxations. Non-collinear spin polarized ionic relaxations, band structure, and density of states calculations were performed for all magnetic conformations considered for monolayers, and for the most stable conformation for the bulk structure, with spin-orbit coupling included.

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**Author Contributions**

R.A.M and J.R.L. designed this project with assistance from L.E.D. R.A.M. synthesized the materials, analyzed the X-ray diffraction data, collected and analyzed IR, UV-Vis-NIR, X-ray photoemission spectra, as well as collected and analyzed variable-temperature conductivity data and magnetometry data with initial guidance from L.E.D and M.E.Z. E.A.P. and J.B.N. completed theoretical computations. E.W.Z. and J.J.U. collected and analyzed thin film conductivity and thermopower measurements. M.W.M., D.J.L., and D.K.S. collected and analyzed X-ray absorption spectra. R.A.M and J.R.L. wrote the manuscript, and all authors contributed to manuscript revision.

**Competing interests**
The authors declare no competing interests.
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Figures:

**Fig. 1: Structural Characterization of Mn$_3$(C$_6$S$_6$).** **a.** Synchotron powder X-ray diffractogram of Mn$_3$(C$_6$S$_6$), with simulated peaks from the $ab$ plane as reference. **b.** Structure of the $ab$ plane of Mn$_3$(C$_6$S$_6$). Teal, yellow, and gray spheres represent Mn, S, and C atoms, respectively.
**Fig. 2 | Calculated band structure and density of states of Mn$_3$(C$_6$S$_6$).** Representative band structure of bulk Mn$_3$(C$_6$S$_6$) with a canted antiferromagnetic spin configuration (left) and corresponding density of states (right). Various canted antiferromagnetic spin configurations give nearly identical band structures (see Supplementary Fig. 11). The plots are results from density functional theory calculations, using an optimized structure (see Computational Methods and Supplementary Figure 10).
Fig. 3 | Magnetic susceptibility data for Mn$_3$(C$_6$S$_6$). a, Field-cooled (under 200 Oe, teal) and zero field-cooled (red) molar magnetic susceptibility data for Mn$_3$(C$_6$S$_6$) collected between 2 and 300 K under an applied field of 200 Oe. b, Variable temperature molar in-phase ($\chi''$) and out-of-phase ($\chi'''$) ac susceptibility data for Mn$_3$(C$_6$S$_6$) collected at the indicated frequencies under a dc field of 25 Oe to reduce noise. Smoothed lines are guides for the eyes, while the vertical lines for 1 and 1000 Hz highlight the frequency dependence.
**Fig. 4 | Spin glass behavior of Mn₃(C₆S₆).**  

a, Illustration of memory dip experiment protocol. The material was first cooled from 30 to 10 K under zero field and held for 10 min; cooled to 8 K and held for 10 min; cooled to 6 K and held for 10 min; and finally cooled to 2 K. A 100 Oe field was then applied and the susceptibility trace was collected upon warming.  
b, Data from thermal memory effect experiments. The red trace displays the ZFC curve after following the protocol illustrated in a. Memory dips at 10, 8, and 6 K are consistent with the thermal annealing protocol. The black trace displays standard ZFC data collected under 100 Oe in the absence of the memory dip protocol. Lines are guides for the eye. (Inset) Difference plot between red and black curves.  
c, Illustration of thermoremanent relaxation experiment. The material was first cooled under a 100 Oe applied field and held for a designated wait time, $t_w$, at 2 K; the field was then removed and the thermoremanent magnetization data were collected.  
d, Thermoremanent magnetization data collected from the protocol in c with different colors indicating designated wait times. The magnetization clearly increases with longer wait times. Solid lines are fits to the curves as described in the Supplementary Information. (Inset) Expanded view between 0 and 10 min highlighting the magnetic ageing characteristic of spin glasses.
Fig. 5 | Variable field magnetization data for Mn₃(C₆S₆). a, Data collected after cooling under 1 T (red curve), −1 T (blue curve), and zero field (black curve). The hysteresis loops collected under applied fields exhibit symmetric shifts relative to the zero-field loop. b, Expanded view of the region between −0.25 and 0.25 T in Fig. 4a. c, Hysteresis data obtained after cooling under 1 T and a 1-h waiting period at zero field. The observed exchange bias is similar to that in a (red curve). (Inset) Expanded view of the exchange bias intercepts. d, Isothermal exchange bias. The sample was cooled under zero field and a field of 1T was then applied for 1 h. (Inset) Expanded view of the exchange bias intercepts. All data was collected at 2 K.
Fig. 6 | Glassy topological dynamics of Mn₃(C₆S₆). a, Derivatives of 2 K thermoremanent magnetization decay curves collected at the indicated waiting times. Curves overlay. b, Illustration of temperature cycling experiment. The sample was cooled from 30 to 2 K under an applied field, held for $t_{w1} = 1500$ s, heated to 4 K and held for 60 s, and then cooled to 2 K and held for $t_{w2} = 300$ s. The field is then set to zero and the thermoremanent magnetization decay curve is collected. c, Data resulting from the temperature cycled aging experiment illustrated in b (red curve). Data collected after 300 and 1500 s wait times (absent cycling) are shown for comparison in purple and blue, respectively. Temperature cycling does not reset the initial state of the glass, as the red curve lies above the purple curve. (Inset) Expanded view of the magnetization decay curves between 2 and 10 min. d, $\chi_3$ versus $T$ data. The peak at ~12 K is consistent with the freezing temperature observed in the ac and dc magnetic susceptibility data.
The data indicate significant spin correlations far above the freezing temperature. Smoothed lines are guides for the eyes.
Magnetic measurements

The exchange bias field, $H_E$, was determined by taking the average of the field-intercepts, and the coercivity was found by calculating the difference between the absolute values of the field-intercepts and dividing by two. In any field cooled exchange bias hysteresis loop measurement, the field strength used to field cool is set as the maximum applied absolute field in the hysteresis measurement (i.e., after field cooling at 1 T, the hysteresis curve is measured between $+/−1$ T).

Magnetization relaxation data were best fit using the stretched exponential decay function $M(t) = M_0 \exp(-t/\tau)^{1−n}$. Alternative decay functions, namely algebraic [$M(t) = M_0 t^{-\alpha}$], logarithmic [$M(t) = M_0 − S \ln(t)$], or Debye exponential relaxation [$M(t) = M_0 \exp(-t/\tau)$] functions, did not result in acceptable fits for the observed relaxation behavior. The more parameterized stretched exponential functions $M(t) = M_0 \exp(-t/\tau)^{1−n} + S \ln(t) + M_0$ or $M(t) = M_0 \exp(-t/\tau)^{1−n}$ gave fits that indicated that the excess parameters were not necessary: the functions collapsed to the same values found for the simple stretched exponential decay function, absent the excess parameters. These alternative glassy dynamic functions were developed to better describe the anomalous response associated with clustered dynamics in disordered glasses: in a geometrically frustrated glass, it is unsurprising that these parameters are unnecessary.

The following protocol was used to extract $\chi_3$. The sample was cooled from 50 K under zero field, pausing at each temperature point shown in Figure 6d of the main text. At each temperature, a magnetization curve was measured, sweeping the field from 0 to 2 T and back again. The magnetization, $M$, in a material with broken time reversal symmetry (such as a spin glass) can be expanded in odd powers of the applied magnetic field, $M(H) = \chi_1 H - \chi_3 H^3 + \chi_5 H^5 \ldots$ from which the linear and nonlinear susceptibility terms can be extracted. Briefly, the linear susceptibility, $\chi_1$, can be extracted by a simple linear fit to the $M(H)$ curves at low fields, where higher order susceptibility terms are minimal. The nonlinear susceptibility, $\chi_{nl}$, can be then extracted and plotted as $\chi_{nl} = \chi_1 - M/H$, after which $\chi_3$ can be extracted by the same linear fitting process after plotting $\chi_{nl}$ versus $H^2$. Curves were fit below 500 Oe ($\chi_1$) and 1100 Oe ($\chi_3$) to ensure...
that the resultant susceptibility did not contain significant contributions from higher order susceptibility terms. Example data and fits are shown in Supplementary Figure 20.

Discussion of the Possibility of Minor Loops in Mn$_3$(C$_6$S$_6$)

The observed magnetic training effect, temperature dependence of the horizontal hysteretic shift, and large increases in coercivity upon field cooling described in this work for Mn$_3$(C$_6$S$_6$) strongly support the presence of exchange bias in this system. However, it is relevant here to comment on minor loop phenomena. In particular, a minor loop, collected after cooling of a material under field, may be shifted due to the presence of magnetic domains that are too large to be flipped by the external field. Indeed, in certain cases minor loops have been incorrectly conflated with exchange bias. However, given that it is possible to isothermally induce exchange bias in Mn$_3$(C$_6$S$_6$) (Fig. 5d, main text), it is clear that the behavior observed here is not the result of such a thermally-mediated effect.

The variable field magnetization curves obtained after cooling under applied fields are shifted significantly off of the ZFC data polarized to an equivalent field, a behavior also at odds with a simple minor loop effect. More generally, the lack of magnetic saturation and field dependence of the bias field observed in Mn$_3$(C$_6$S$_6$) are similar to canonical spin glasses as well as other single-phase exchange bias materials. Further, we note that the field dependence of $H_C$ and $H_E$ are dissimilar (Supplementary Figure 14), inconsistent with what is expected due to a minor loop phenomenon: if minor loops were responsible for the observed shifted loops, this dependence would be significantly more symmetric.

While we believe the foregoing points are sufficient to obviate concerns regarding conflating a minor loop phenomenon for exchange bias in the Mn$_3$(C$_6$S$_6$), we include a more semantic discussion as well. To do so, we first invoke the phenomenon of an “effectively” saturated system. An effectively saturated system occurs when the maximum applied field is larger than the anisotropy field of the material, and as a consequence, should no longer exhibit a shifted minor loop artifact due to thermally pinned domains. The experimentally derived anisotropy field of isoelectronic potassium iron jarosite is far below the maximum applied fields used in this study, which suggests that the shift in the hysteretic origin observed for Mn$_3$(C$_6$S$_6$) cannot be attributed to a minor loop phenomenon. Indeed, if the observed behavior were due to a minor loop phenomenon, this would suggest that a material containing isotropic, high spin manganese(II) is capable of inducing anisotropy fields above 7 T, which is unreasonable given the likely weak spin-orbit coupling and lack of unquenched orbital angular momentum in our material.

A further consequence of our discussion of effective major and minor loops is that a system is effectively saturated (and thus in the effective major loop) if the hysteretic traces for increasing and decreasing fields coalesce. As is apparent in the zero-field cooled hysteresis loops presented in Fig. 4 and Supplementary Figure 13, the loops are effectively closed prior to the maximum field applied for field-cooled measurements. In contrast to the zero-field cooled loops, the field cooled loops are significantly wider. In context, this difference suggests that the anisotropy field is asymmetrically strengthened by cooling under a field, an interpretation that is broadly consistent with our discussion of chiral induction in the main text.

One other possible explanation for this isothermal behavior is the dynamics of this system, but it can be seen that the dynamics of Mn$_3$(C$_6$S$_6$) are also not responsible for the bias. In particular, magnetization decay curves for Mn$_3$(C$_6$S$_6$) after cooling under a larger field 1 T are
independent of $t_w$ (Supplementary Fig. 21), as expected in spin glasses. If relaxation was responsible for the hysteretic shift, sweeping to an applied field of the opposite polarity ($-1$ T) would reset the magnetic state and result in the zero field-cooled (ZFC) loop. The fact that an exchange bias is instead observed strengthens the case for the more subtle explanation of a dynamic chiral induction of spin texture. Our experiments detailing field annealing with variable time are clear evidence here (Supplemental Fig. 18), as the only difference between the measurements is time: the initial magnetization does not increase, while the exchange bias does. Additionally, we note that if simple relaxation were a sufficient explanation for the isothermal bias, we would expect to see drastically different behavior in the magnetic training effect: both the left and right hysteretic intercepts should trend toward the ZFC loop if the shifted hysteresis loop was evidence only of dynamic behavior.
Supplementary Figure 1: Thin film of Mn$_3$(C$_6$S$_6$) deposited on a glass substrate.

Supplementary Figure 2: Scanning electron microscopy images of Mn$_3$(C$_6$S$_6$). a. Smooth surface observed at the organic/aqueous interface. b. Rough underside of the thin film, displaying crystallites of Mn$_3$(C$_6$S$_6$).
Supplementary Figure 3: a. Simulated powder X-ray diffraction patterns for models of eclipsed and staggered conformations of Mn₃(C₆S₆) generated in Materials Studio, compared with the experimental data. b. Materials Studio models of the eclipsed and staggered conformations.

Supplementary Figure 4: Transmission (blue) and attenuated total reflectance Fourier transform infrared (gold) spectra of Mn₃(C₆S₆). Transmission IR data were collected taken in a nujol matrix pressed between polished NaCl optical plates. Starred peaks in the transmission data correspond to peaks from nujol, and the data demonstrate that the nujol peaks do not obscure Mn₃(C₆S₆) peaks.
Supplementary Figure 5: Portions of the high-resolution X-ray photoemission spectrum of Mn₃(C₆S₆). Experimental data are given as black dots, and black lines indicate the composite fit. Red lines in 5a represent peaks associated with spin orbit decoupled peaks, while blue lines designate the same in 5d. Red line in 5d represents a satellite peak. a. Sulfur 2p, b. sulfur 2s, c. carbon 1s, and d. manganese 2p spectral regions.
Supplementary Figure 6: X-ray absorption near edge structure (XANES) spectra of Mn$_3$(C$_6$S$_6$) and MnS, with derivatives shown in the inset. The overlap of the derivative spectra indicates that MnS is a good model for the oxidation state of Mn centers in Mn$_3$(C$_6$S$_6$).

Supplementary Table 1: Conductivity ($\sigma$) values and Seebeck coefficients determined from measurements on two thin film samples of Mn$_3$(C$_6$S$_6$). For both films, three continuous domains were visually identified, and then measured 3 times to determine the average conductivities reported.

| Domain  | $R_s$ (kW) | Seebeck coefficient ($\mu$V/K) | Avg. film thickness (nm) | Avg. $\sigma$ (S/cm) | Power Factor ($\mu$W/mK$^2$) |
|---------|------------|------------------------------|--------------------------|----------------------|-----------------------------|
| Domain 1 | 127        | 169                          | 245                      | 0.32                 | 0.92                        |
| Domain 2 | 33.99      | 166                          | 199                      | 1.48                 | 4.08                        |
| Domain 3 | 1469       | 165                          | 219                      | 0.03                 | 0.08                        |
| Average |            | 167                          | 0.61                     | 1.69                 |                             |

| Domain  | $R_s$ (kW) | Seebeck coefficient ($\mu$V/K) | Avg. thickness (nm) | Avg. $\sigma$ (S/cm) | Power Factor ($\mu$W/mK$^2$) |
|---------|------------|------------------------------|---------------------|----------------------|-----------------------------|
| Domain 1 | 332.9      | 109                          | 192                 | 0.16                 | 0.19                        |
| Domain 2 | 270.8      | 109                          | 125                 | 0.3                  | 0.35                        |
| Domain 3 | 912.6      | 117                          | 190                 | 0.06                 | 0.08                        |
| Average |            | 112                          | 0.173               | 0.21                 |                             |
**Supplementary Figure 7:** a. I-V curves of a pressed pellet of Mn$_3$(C$_6$S$_6$) at various temperatures. b. Fit to Efros-Shklovskii variable range hopping model (see Ref. 44 in Methods section of main text).

**Supplementary Figure 8:** Powder X-ray diffraction pattern obtained on a pressed pellet of Mn$_3$(C$_6$S$_6$). Comparison of the data with the diffraction pattern of the as-synthesized material suggests that the pressed pellet undergoes a pressure induced phase change to the staggered stacking conformation. This highlights the necessity of single crystal and/or film measurements.

**Supplementary Figure 9:** Diffuse reflectance UV–Vis–NIR spectrum of
Mn$_3$(C$_6$S$_6$). The diffuse reflectance UV–Vis–NIR spectrum of Mn$_3$(C$_6$S$_6$) (Supplementary Fig. 7) displays broad features centered at 24000 and 32500 cm$^{-1}$, which were assigned to charge-transfer and π-π$^*$ ligand-based transitions, respectively, consistent with the benzenehexathiolate species$^{20}$. 
Supplementary Figure 10: DFT optimized eclipsed structure used for bulk band structure and DOS calculations, (ab plane on left, stacking conformation on right). Optimized structure has a unit cell of $a = b = 9.1518$ Å, $c = 8.56602$ Å (double the interlayer distance), in reasonable agreement with experimental values.
Supplementary Figure 11: Temperature dependence of the molar magnetic susceptibility times temperature, $\chi M T$, for $\text{Mn}_3(C_6S_6)$ under $H_{dc} = 1000$ Oe. Dotted line shows expected value for uncoupled Mn(II) cations (13.13 emu·K /mol). The experimental data indicates a compensated moment of only 6.94 emu·K /mol at room temperature, indicating local antiferromagnetic interactions are persistent even at elevated temperatures.

Supplementary Figure 12: Curie-Weiss fit of $\text{Mn}_3(C_6S_6)$. Data taken with an applied field of 1000 Oe. Data was fit to $\chi_M = C/(T - \Theta)$, where $C$ is the Curie Constant, $\Theta$ is the Weiss constant, and $T$ is temperature.
**Supplementary Table 2:** Parameters derived from fitting thermoremanent magnetization decay curves collected after cooling a sample of Mn$_3$(C$_6$S$_6$) from 30 to 2 K under 100 Oe and holding for various wait times, $t_w$ (see Fig. 3d in the main text). The resulting magnetization curves were fit to a stretched exponential as specified above.

| $t_w$ (min) | $M_0$ ($\mu_B$) | $\tau$ (s) | $n$   |
|-------------|-----------------|------------|-------|
| 1           | 7.73×10$^{-4}$  | 1.00×10$^{11}$   | 0.829 |
| 10          | 7.74×10$^{-4}$  | 5.71×10$^{10}$   | 0.822 |
| 30          | 7.735×10$^{-4}$ | 2.868×10$^{10}$  | 0.812 |
| 60          | 7.743×10$^{-4}$ | 2.868×10$^{10}$  | 0.812 |
**Supplementary Table 3:** (Upper) Comparison of energies of various spin conformations of Mn$_3$(C$_6$S$_6$). (Lower) Monolayer band structure of the lowest energy antiferromagnetic configuration.

| Energy relative to most stable conformation (eV/atom) | Band Gap (eV) |
|-----------------------------------------------------|---------------|
| Ferromagnetic                                        | 7.839         |
| Ferrimagnetic                                        | 0.956         |
| Non-collinear AFM 1                                  | 0.005         |
| Non-collinear AFM 2 (all-in-all-out)                 | 0.000         |
| Non-collinear AFM 3                                  | 0.421         |

![Diagram showing spin configurations and band structure]
Supplementary Figure 13: Zero-field cooled magnetic hysteresis data collected for Mn$_3$(C$_6$S$_6$) at 2 K.

Supplementary Figure 14: a. Change in the values of $H_C$ and $H_E$ with successive hysteresis cycles. Hysteresis data were collected after cooling under 1 T. Data for loops 1-7 were then collected in succession. Solid lines are guides for the eyes. b. Representative training loop data. The material was cooled at 1 T, and multiple hysteresis loops were taken afterward.
Supplementary Figure 15: Field dependence of exchange bias and coercive fields at 2 K. Solid lines are guides for the eyes.
Supplementary Figure 16: Temperature dependence of exchange bias field. The solid line is a guide for the eye. The profile of this trace is consistent with exchange biased systems."
Supplementary Figure 17: Field dependence of the leftmost hysteresis loop intercept as a function of cooling field.
Supplementary Figure 18: Variable-field magnetization data collected after zero-field cooling and subsequently annealing under a 1 T field for 30 sec (blue) and 5 min (red). **a.** Overlap of both loops. **b.** Initial magnetization of the two loops. **c.** Expanded view of the observed exchange bias under both protocols. **d.** Expanded view of leftmost intercept, revealing an increase of 25 Oe between the 30 sec and 5 min data. This increase corresponds to a 14% increase in observed exchange bias.
Supplementary Figure 19: Here, we provide an additional demonstration of the viability of geometric frustration toward engendering exchange bias. We synthesized hydronium iron jarosite, a prototypical topological spin glass, via established literature methods. The material was cooled under various fields and variable field magnetization data were collected subsequently, akin to the procedure followed for Mn₃C₆S₆. a. Structure of hydronium iron jarosite as determined in supplementary reference 20. The material was synthesized via established literature methods. b. The maximum exchange bias ($H_E = 1340$ Oe) was observed after cooling under a 4 T field.

Supplementary Figure 20: a. Example magnetization isotherms used to extract the non-linear susceptibility, $\chi_{nl}$, for Mn₃C₆S₆. b. $\chi_{nl}$ versus $H^2$ curves used to extract $\chi_6$. An example fit is shown. Fit line was extended for clarity.
Supplementary Figure 21: Thermoremanent relaxation curves for Mn$_3$C$_6$S$_6$ after cooling under a 1 T field with different $t_w$. The black line is a stretched exponential fit to the data.
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