Supplementary Information to “Realization of a three-dimensional spin-anisotropic harmonic honeycomb iridate”

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Supplementary Figure 1. X-ray diffraction pattern in the \((h0k)\) (top) and \((h1l)\) (bottom) planes. Raw data (AB) is well reproduced by calculations (CD) for the \(Cccm\) structure (Table I), in contrast an \(Fddd\) (hyper-honeycomb) structure (EF) can only explain the existence of less than half of the observed diffraction peaks.
Supplementary Figure 2. Observed diffraction intensities plotted against those calculated in the refined (A) $Ccmm$ (Table I) and (B) $Fddd$ structural models. The dashed lines indicate 1:1 agreement between data and model and error bars reflect the intensity uncertainties after averaging the observed intensities of reflections expected to be equivalent under orthorhombic symmetry. The three families of reflections discussed in the text are plotted as different symbols/colors (black circles, red squares, and blue triangles). Note that the $Fddd$ model predicts zero intensity at the observed (odd, odd, even) reflections and largely overestimates the intensities of (odd, odd, odd) peaks.
**Supplementary Figure 3.** Crystal structure models described in the text, (A) \(Cccm\) (Table I) and (B) \(Fddd\), large brown balls - Ir, medium light gray balls - Li, small gray balls - O.
Supplementary Figure 4. Preliminary measurements of the change in the lattice parameters along the crystallographic $a$, $b$ and $c$ direction on cooling below the magnetic transition at $T_N$. We do not observe any changes in the crystallographic symmetry, but the elastic response in each direction is highly anisotropic, with the $b$-axis changing roughly 10 times more that the $a$-axis.
Supplementary Figure 5. The magnetic anisotropy extracted from the low field slope of the torque signal $\tau/\mu_B H$, similar to that shown in Figure ?? B, taken for rotations through the three principal crystallographic planes and at different temperatures. The anisotropy is shown in units of $\mu_B$ per Ir, for (A) the $\chi_a - \chi_b$, (B) $\chi_a - \chi_c$ and (C) $\chi_b - \chi_c$. The only change of sign in the anisotropy is in (A) and an enlargement of this scale is shown in Figure 3D of the main text to emphasize this.
Supplementary Figure 6. Torque signal taken at magnetic fields up to 35 T at the National High magnetic Field Laboratory. The field $H^*$ is extremely clear at all angles. At angles away from the principal axes the torque signal is very clearly linear and follows a $\sin 2\theta$ dependence described by equation 4. The larger asymmetry in this data set compared to that measured in the superconducting magnet, is due to the larger field gradient experienced by the sample.
Supplementary Figure 7. (A) The two choices of edge shared bonds give rise to two kinds of links that are locally indistinguishable. These define two bonding planes (see Figure 3A of the main text) that are an angle $\phi_o \sim 70^\circ$ apart. (B) Links along the $c$-axis can either keep the same ($S$-links) or rotate ($R$-links) the honeycomb planes.
**Supplementary Figure 8.** The harmonic honeycomb family is rich in structural possibilities that tune symmetry (depending on whether the number of $N_R$ and $N_S$ links is odd or even) and dimensionality (the extent of the $N_S$ links). This table summarizes this observation. Note we assume that the IrO$_6$ octahedra have ideal cubic symmetry. Complex distortions may create systems of lower symmetry than that indicated.
II. SUPPLEMENTARY TABLES

Supplementary Table I. Fractional atomic coordinates for $H\langle 1\rangle$-Li$_2$IrO$_3$ extracted from single-crystal x-ray data at 300 K ($Cc_m$ space group, $a = 5.9119(3)$ Å, $b = 8.4461(5)$ Å, $c = 17.8363(10)$ Å, $Z = 16$). All sites are fully occupied and Li positions are fixed to nominal values such that edge-sharing IrO$_6$ and LiO$_6$ octahedra form a near-hexagonal arrangement in both $(a + b, c)$ and $(a - b, c)$ planes. The isotropic displacement parameter $U$ for Li is also fixed to a value in the range found for the other atoms. Values in brackets show standard deviations in the fitted parameters.

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III. SUPPLEMENTARY DISCUSSION

A. Single Crystal Refinement

The very different magnetic ordering temperature of our flux-grown single crystals, $T_N = 38$ K, compared to 15 K [1] reported for the so-far-synthesized powders of Li$_2$IrO$_3$ (layered honeycomb crystal structure, monoclinic $C2/m$ unit cell [2]) suggested that the flux-grown...
samples may realize a polytype of Li$_2$IrO$_3$ with a different crystal structure. This was clearly revealed by x-ray diffraction measurements performed using a Mo-source Oxford Diffraction Supernova diffractometer. Several crystals were measured and the diffraction patterns were all consistent in terms of the unit cell and selection rules for the observed diffraction peaks. Here we report in detail the data on an approximate rhombus-shaped $\sim 35 \times 10^3 \mu m^3$ flux-grown crystal.

The lattice parameters of the monoclinic layered honeycomb crystal structure [2] could not account for the positions of over 2000 Bragg peaks measured in our diffraction experiment, which instead could be indexed with an orthorhombic unit cell with parameters given in Table I. Representative diffraction patterns are illustrated in Fig. 1AB, where $(h,k,l)$ refer to wavevector components in reciprocal lattice units of the orthorhombic unit cell. The highest-symmetry orthorhombic space groups that can account for all of the observed peaks in the diffraction patterns are $Cccm$ (no. 66) and $Ccc2$ (no. 37). Both have the same selection rule for allowed reflections for a general atomic position, $(hkl) : h + k$ even, $(0kl) :$ both $k$ and $l$ even, $(h0l) :$ both $h$ and $l$ even. Both have a $C$-centered unit cell, corresponding to a translation of $(\frac{1}{2}, \frac{1}{2}, 0)$, and $Ccc2$ is obtained from $Cccm$ by removing a mirror plane normal to the $c$-axis. In the final refinements of the crystal structure reported below, we did not find any significant atomic displacements and correspondingly no improvement in the goodness of fit when the crystal symmetry was lowered from $Cccm$ to $Ccc2$, so in the following we discuss only the higher symmetry case.

The unit cell volume is approximately $4 \times$ the unit cell volume of the layered honeycomb structure ($Z = 4$), which suggested that the present polytype has the same mass density, but with $Z = 16$ formula units per unit cell. Since iridium is by far the dominant x-ray scatterer with 77 electrons (oxygen 8 and lithium 3 electrons), we first attempted a preliminary fit to the x-ray data assuming a simplified structural model composed solely of Ir ions located in general positions within the $Cccm$ space group symmetry. The iridium coordinates were set free to refine within the bounds of the orthorhombic unit cell. Remarkably, the refinement easily converged with Ir ions occupying two crystallographic sites with coordinates close to those listed in Table I. To test that this solution was reliable, and not an accidental local minimum in the least squares refinement, we employed simulated annealing techniques implemented in FullProf [3] to explore the full parameter space of the structural model against the full data set (treating each observed $(h,k,l)$ reflection as an independent data
point without imposing any symmetry constraints). By constructing a lattice with the dimensions of the orthorhombic unit cell $a \times b \times c$ but with lowered symmetry $P\bar{1}$, and populating it with eight iridium ions with atomic fractional coordinates free to vary within the full unit cell according to the annealing process, we found an unconstrained (except for inversion symmetry) yet highly reproducible iridium lattice that corresponded to a global minimum in the parameter space. This structure was found to be in perfect agreement with the iridium framework of the initial refinement, confirming both the structural model and the space group, $Cccm$. In addition, the choice of space group symmetry was subjected to more rigorous testing by simulated annealing, which was systematically performed under symmetry constrains corresponding to sub-groups of $Cccm$ and $Fddd$ (see below), all of which converged to the $Cccm$ solution or failed, respectively.

Using the measured Bragg peak intensities, space group symmetry, and the identified iridium positions, we calculated the electron density maps in the unit cell (using Shelxl [4] and Wingx [5]). This revealed additional electron density pockets, which we identified as the location of oxygen ions. Lithium ions scatter x-rays very weakly (only 3 electrons) and their positions cannot be reliably identified using x-ray scattering techniques, especially in the presence of heavy elements such as iridium. However, assuming that the fundamental building blocks of the structure are edge-sharing IrO$_6$ and LiO$_6$ octahedra (as in the honeycomb polytype), one can readily determine idealized lithium positions (listed in Table I and shown in Fig. 3A) required to achieve this connectivity.

Assuming lithium ions to be fixed at the ideal positions, a full structural model was refined against the data set using FullProf [3]. Iridium and oxygen ions were located in the initial positions determined above, and their atomic coordinates were set free to vary within the constraints of $Cccm$ crystal symmetry. It became apparent that the structural model gave an excellent fit to most reflections, but over-estimated the diffraction intensity of a small subset. Specifically, the empirically-determined selection rules for observed ($h,k,l$) reflections give three families: (even, even, even) with $h+k+l = 4n$, $n$ integer, (odd, odd, odd) except $l = 3 + 6n$, $n$ integer, and (odd, odd, even). The intensities of these families of peaks are plotted in Fig. 2A against the model calculation. It is clear that the model is in excellent agreement with the (even, even, even) and (odd, odd, odd) reflections. The model also explains the presence of the third family of reflections, the (odd, odd, even), but the observed intensity is weaker than predicted. In fact those reflections showed an asymmetry in the intensity
not expected under orthorhombic symmetry, i.e. $I_{(\text{odd,odd,even})} \neq I_{(-\text{odd,odd,even})}$ (Fig. 2A only shows the averaged (reduced) intensity of those reflections with the error bars indicating the spread of values). The degrees of both the lowered average intensity and asymmetry were found to vary across a number of different samples measured, however, the excellent agreement to the (even, even, even) and (odd, odd, odd) reflections was robust and consistent across all samples tested. We propose that the discrepancies in (odd, odd, even) intensities are most likely due to sample-dependent structural stacking faults, as discussed later in this section. A final refinement was performed against the (even, even, even) and (odd, odd, odd) reflections with excellent reliability factors $R_F^2 = 3.83\%$, $wR_F^2 = 4.91\%$, and $R_F = 2.27\%$ [including also the (odd, odd, even) reflections in the refinement resulted only in very small changes in the oxygen positions, which we regard to be below the accuracy that can be reliably determined]. The obtained structural parameters from the final refinement are given in Table I; essentially the same results are obtained in refinement done using Sir-92 [6] and Shelxl [4]. The above refinement assumed stoichiometric Li$_2$IrO$_3$ with all atomic positions fully occupied. However, we have also tested for the possibility that each of the seven cation sites (Ir1-2, Li1-5) could have a mixed Li/Ir occupancy. In this test we constrain the total site occupancy to unity (i.e. no structural vacancies) with no constraint on the total Li:Ir atomic ratio (i.e. stoichiometry free to vary). Under these constraints a full refinement of Li/Ir occupancies on the cation sites lead to no significant improvement in the refinement parameters. Furthermore, the occupancies of the Li and Ir sublattices refined to their nominal values (Li only in Li1-5 sites and Ir only in Ir1-2 sites) within an error of less than 3\%, further confirming the stoichiometric composition and the structural model in Table I. The obtained crystal structure is illustrated in Fig. 3A. The full 3D x-ray diffraction pattern observed is well accounted for by this model and representative plots are shown in Fig. 1CD. The refined structure has IrO$_6$ octahedra distorted from ideal cubic with non-equivalent Ir-O distances spanning a range of up to $\sim 7\%$ for each octahedron, comparable to the range of Ir-O distances reported for the IrO$_6$ octahedra in the layered honeycomb polytype [2].

The resulting Ir network shown in Fig.1B-C of the main text is a novel arrangement of near-ideal honeycombs in three dimensions not reported before as far as we know in other 3d or 5d oxides. Ir honeycombs form parallel rows that alternate along the two diagonals of the unit cell in the $ab$ plane, namely along $\mathbf{a} + \mathbf{b}$ at $z = 0$ and along $\mathbf{a} - \mathbf{b}$ at $z = 1/2$. 
This alternation leads to a 3D network of inter-connected honeycomb rows stacked along the $c$-axis, where all nearest-neighbor Ir-Ir links are nearly the same length ($\sim c/6$) and all Ir-Ir-Ir bond angles are close to 120°. The Ir positions are indeed very close to such an ideal lattice realized for Ir1 at $8k$ ($1/4, 1/4, 1/12$), Ir2 at $8i$ ($1/2, 1/2, 1/6$) and $c = \sqrt{3(a^2 + b^2)}$, compare with Table I where the latter equation is satisfied to within 0.1%. This near-regularity of the Ir lattice is directly manifested in the observed x-ray diffraction pattern by a conspicuous absence of detectable scattering intensity along the $c$-axis for $l = 3 + 6n$, $n$ integer as illustrated in Fig. 1B, this is not due to a general symmetry-imposed selection rule of the space group, but is due to a near cancellation of intensity for a lattice built out of near-ideal honeycomb sections stacked along the $c$-axis.

The obtained iridium lattice can be thought of as being the $N = 1$ member of a regular series of periodic structures of alternating honeycomb sections of different widths ($N = 1, 2, 3 \ldots \infty$) as illustrated in Fig. 5B of the main text, with the layered honeycomb polytype ($C2/m$) being the $N = \infty$ end member. The $N = 1$ structure could be “transformed” into the honeycomb polytype by selectively mirror-imaging in the $bc$ plane the iridium honeycomb rows centered at $z = 1/2$. In this case, iridium ions form infinite honeycomb layers in the $(a + b, c)$ plane and the unit cell along $c$ is halved. It is clear from this construction why the reported repeating unit cell dimension of the layered honeycomb structure along this direction (labelled as $b_m = 8.9294$ Å in the standard monoclinic cell notation [2]) is nearly half that of the $c$-axis repeat of the $N = 1$ polytype, $c = 17.8363(10)$ Å, reported here.

For completeness we note that the different polytypes in the series plotted in Fig. ??B could be easily distinguished experimentally, as they have different symmetries and/or different unit cell sizes, and consequently distinct diffraction patterns. For illustration we consider the $N = 0$ hyper-honeycomb[7, 8] shown in Fig. ??B, $H\langle 0 \rangle$. The periodic iridium atomic arrangement can be described by an orthorhombic unit cell of the same size $a \times b \times c$ and orientation of axes as for $N = 1$, but face-centered and with diamond glide planes. In the corresponding space group, $Fddd$ (no. 70), iridium ions occupy a single crystallographic site, $16g$ (0, 0, $z$) (origin choice 1), with $z = 1/12$ assuming the $c$-axis Ir-Ir bond length is $c/6$.

Fig. 1AB and EF show the comparison between data and the calculated diffraction pattern for a generic hyper-honeycomb structural model constructed such as to have hexagonal layers of edge-sharing IrO$_6$ and LiO$_6$ octahedra in the $(a \pm b, c)$ planes and 90° O-Ir-O and O-Li-O
bonds. The atomic coordinates considered are Li1 16g (0, 0, 1/4), Li2 16g (0, 0, 5/12), O1 32h(1/4, 0, 1/6), O2 16e (1/4, 0, 0) and the full structure is plotted in Fig. 3B. As illustrated in Fig. 1EF the $F_{ddd}$ space group has a much more restrictive selection rule for allowed reflections compared to $C_{ccm}$, for example in the $(hk0)$ plane $h + k$ is required to be a multiple of 4 and both $h$ and $k$ to be even, as opposed to the less restrictive $h + k$ even for $C_{ccm}$, and for $(h1l)$ both $h$ and $l$ odd, as opposed to $h$ odd and $l$ unrestricted for $C_{ccm}$. The $C_{ccm}$ selection rules can account for all the experimentally observed reflections, whereas an $F_{dd}d$ unit cell could not account for the presence of the (odd, odd, even) reflections, such as the relatively strong (110), see Fig. 1AE. Furthermore, refinement of the $F_{dd}d$ structure against the intensities of reflections allowed in this symmetry, namely (even, even, even) and (odd, odd, odd), gives a statistically rather poor fit with $R_{\text{F}} = 21.4\%$, $wR_{\text{F}} = 36.2\%$, and $R_{\text{F}} = 13.3\%$. This becomes clear when comparing the calculated intensities to those observed, shown in Fig. 2B. The $F_{dd}d$ model only reproduces the correct intensities for the (even, even, even) reflections, whereas the intensities of the (odd, odd, odd) reflections are calculated to be approximately double that observed. For completeness, the additional family of (odd, odd, even) reflections observed in the experimental data are also shown in Fig. 2B, wrongly predicted to have exactly zero intensity in the $F_{dd}d$ space group. These results, coupled with the conclusions drawn from the simulated annealing tests, conclusively show that the hyper-honeycomb $F_{dd}d$ structural model (and lower-symmetry structures obtained by small distortions of an $F_{dd}d$ parent structure) can be ruled out for the single crystals reported in this study.

Finally, we note that in addition to sharp Bragg peaks the x-ray diffraction pattern also revealed the presence of weak, but clearly visible diffuse scattering in the form of “rods” of scattering intensity in-between Bragg peaks along the $l$-direction, sharply defined in the $h$ and $k$ directions, as clearly seen in Fig. 1B with the selection rule $h$ odd and $k$ odd. Whilst a quantitative refinement of the data including the diffuse scattering is beyond the scope of this present study, we propose that this diffuse scattering most likely originates from occasional structural faults in the nominal $C_{ccm}$ atomic stacking sequence along the $c$-axis. The presence of diffuse scattering takes intensity away from the sharp Bragg peaks, and it is possible that some families of Bragg peaks are affected more than others; this might explain why the intensity of one particular family of reflections, namely the (odd, odd, even) peaks located on the diffuse scattering rods, appears weaker in experiment than predicted by a
structurally-perfect $Cccm$ model considered in our refinement, see Fig. 2A (blue triangles).

We have carried out extensive high-resolution SXD measurements at $\sim 8$ K to search signature of lowering of structural symmetry due to magnetic transition. These measurements were performed on the 6-ID-B undulator beamline at Advanced Photon Source using an incident photon energy of 11.215 keV and pyrolitic graphite analyzer. Only resolution-limited Bragg peaks allowed by the proposed space group were observed indicated the structure remained three-dimensionally ordered and fully coherent well below $T_N$. Furthermore, these measurements also ruled out any superlattice peaks (e.g. due to structural modulation, or magnetic order) at half-integer reciprocal-lattice points such as (1/2,0,0), (1/2,1/2,0). The temperature dependence of the orthorhombic lattice parameters around the magnetic transition $T_N = 38$ K was measured using $\theta - 2\theta$ scans to determine the $2\theta$ location of strong structural Bragg peaks (-2,0,6), (0,0,12), and (0,2,14) as a function of temperature between 8.4 - 45.1 K. Preliminary, data in Figure 4 shows a small change of all orthorhombic lattice parameters around the 38 K magnetic transition and relaxation to comparable lattice parameters both below and above the transition. The percent change in lattice parameter appears to be an order of magnitude greater for the $b$-axis than for $a$ or $c$, analogous to magnetic anisotropy seen in the susceptibility data.

B. Magnetic Characterization

A magnetically anisotropic material experiences a magnetic torque when its magnetization is not aligned with the applied magnetic field; the deflection of the cantilever in a uniform magnetic field is hence a direct measure of the magnetic anisotropy,

$$\tau = M \times H.$$  \hspace{1cm} (1)

At small fields, where the magnetic response is linear, the magnetic anisotropy is captured by a susceptibility tensor $\chi_{ij}$.

$$M_i = \chi_{ij}H_j$$  \hspace{1cm} (2)

The tensor is diagonal in the basis of the principal magnetic axes, which defines three principal components of magnetic susceptibility. For an orthorhombic crystal, these magnetic axes naturally coincide with the crystallographic directions, defining $\chi_{a,b,c}$. For example, for rotations in the $b$-$c$ plane, the anisotropic magnetization $(M_b, M_c) = (\chi_b H_b, \chi_c H_c)$ creates a
Defining \( \theta \) as the angle between a crystallographic axis (\( c \) in this case) and the applied magnetic field, the torque can be rewritten as

\[
\tau_a = (\chi_b - \chi_c)H^2 \sin^2 \theta \cos \theta = \frac{(\chi_b - \chi_c)H^2 \sin 2\theta}{2}
\]

From this expression, the magnetic axes can be precisely identified from a complete angular dependence of the torque measurements (Figure 4B of the main text), with the amplitude of the \( \sin 2\theta \) dependence being proportional to the magnetic anisotropy \( \alpha_{bc} = (\chi_b - \chi_c) \). In \( \text{Li}_2\text{IrO}_3 \) the magnetic axes are independent of temperature between room temperature and 1.5 K, but unusually, the sign of the anisotropy between the \( b \) and \( c \) axes, \( \alpha_{bc} \), changes at around 75 K (Figure 4D of the main text).

A convenient way to represent magnetization as observed by torque measurements is by plotting \( \tau/H \) versus \( H \) (Figure 4B of the main text). This figure clearly demonstrates the linear dependence of magnetization at low fields with a slope that follows a \( \sin 2\theta \) dependence with field orientation (colored curves). The softer component of magnetization appears to saturate at a field \( H^* \), above which the linear response (equation 4) is no longer valid. The finite torque at magnetic fields greater than \( H^* \) indicates the finite angle between \( M \) and \( H \) up to the highest measured magnetic fields. \( H^* \) is strongly dependent on the orientation of the crystal with respect to magnetic field. The largest kink field along the crystallographic \( a \) direction was measured at the NHMFL in Tallahassee. The observed overall negative slope at higher fields is due to a force component from a finite magnetic field gradient. A nonlinear torque signal was measured below \( H^* \) for magnetic fields aligned close to the hard susceptibility direction, \( \chi_a \), where the minimal torque condition is an unstable equilibrium (Figure 4B of the main text and Supplementary Figure 6).

In the harmonic honeycomb series each iridium atom occupies a local environment with uniaxial \( g \)-factor anisotropy that can be captured by a magnetic susceptibility \( \chi_\parallel \), parallel to and \( \chi_\perp \), perpendicular to the plane defined by its three nearest neighbor iridium atoms — the interlaced honeycomb planes. The measured high temperature magnetic anisotropy, \( \alpha_{ij} \), arises from the sum of this local anisotropy of the two honeycomb planes revealing that \( \chi_\parallel > \chi_\perp \). Notably this is the opposite of the anisotropy \( \chi_\parallel < \chi_\perp \) observed for the layered
sodium iridate, $^7$H(∞)-Na$_2$IrO$_3$ Ref. 1. Superposition of both honeycomb planes leads to

\[ M_a = M_{\perp} \cos \phi / 2 + M_{||} \sin \phi / 2 \]
\[ M_b = M_{\perp} \sin \phi / 2 - M_{||} \cos \phi / 2 \]  

where the magnetization parallel, $M_{||}$, and perpendicular, $M_{\perp}$, to each of the planes can be written

\[ M_{\perp} = \chi_{\perp} H_{\perp} = \chi_{\perp}(H_a \cos \phi / 2 + H_b \sin \phi / 2) \]
\[ M_{||} = \chi_{||} H_{||} = \chi_{||}(H_a \sin \phi / 2 - H_b \cos \phi / 2) \]  

(5)

Therefore, the geometric relation between the underlying pair of honeycomb planes results in three components of magnetization determined by only two microscopic parameters

\[ M_a = H_a \left[ \chi_{\perp} \cos^2 \phi / 2 + \chi_{||} \sin^2 \phi / 2 \right] \]
\[ M_b = H_b \left[ \chi_{\perp} \sin^2 \phi / 2 + \chi_{||} \cos^2 \phi / 2 \right] \]
\[ M_c = H_c \chi_{||} \]  

(6)

Using $\chi_{\pm} = (\chi_{||} \pm \chi_{\perp}) / 2$ the anisotropic susceptibility of this family of structures can be simplified to

\[ \chi_a = \chi_+ - \chi_- \cos \phi \]
\[ \chi_b = \chi_+ + \chi_- \cos \phi \]
\[ \chi_c = \chi_+ + \chi_- \]  

(7)

As a consequence, at high temperatures where $g$-factor anisotropy dominates, all three principal components of the magnetic susceptibility must order with $\chi_c > \chi_b > \chi_a$. The geometry of the undistorted, edge-sharing octahedra constrains the angle separating these two planes to $\phi = \arccos(1/3) \approx 70^\circ$ (Figure 3A of the main text). The geometric angle $\phi = \arccos 1/3$, which is also reflected in the crystal morphology, is directly apparent in the observed high temperature magnetic anisotropy, where $\chi_{a,b,c}$ are equally spaced,

\[ \chi_a = \chi_+ - \left(1/3\right) \chi_- \]
\[ \chi_b = \chi_+ + \left(1/3\right) \chi_- \]
\[ \chi_c = \chi_+ + \chi_- \]  

(8)

This equal separation is observed as the ratios of the high temperature anisotropies saturating to the values of $\alpha_{ba}/\alpha_{ac} = -1/2, \alpha_{bc}/\alpha_{ac} = 1/2, \alpha_{bc}/\alpha_{ab} = 1$ (see Figure ?? B).
C. Kitaev quantum spin liquid

Every member of the harmonic honeycomb series is bonded by edge sharing IrO$_6$ octahedra. The edge-sharing geometry of the octahedra preserves the essential ingredients of the Kitaev model and this is universal for this family of structures. All three dimensional arrangements of edge-sharing octahedra maintain the interfering Ir-O$_2$-Ir exchange paths, where each of the three nearest neighbor Ir-Ir interactions predominantly couples a particular orthogonal component of spin (see Figure 4A of the main text). In the idealized limit of symmetric octahedra, such changes may compete primarily with the usual rotationally symmetric Heisenberg interactions. In the Kitaev limit where Heisenberg interactions may be set aside, the Hamiltonian becomes a sum of spin-anisotropic exchange terms

$$H_{K} = -K^c \sum_{\langle ij \rangle \in \hat{b}_\perp} S_i^b S_j^b - K^h \sum_{\langle ij \rangle \in (\hat{a} + \hat{c})_\perp} S_i^{\hat{a} + \hat{c}} S_j^{\hat{a} + \hat{c}} - K^h \sum_{\langle ij \rangle \in (\hat{a} - \hat{c})_\perp} S_i^{\hat{a} - \hat{c}} S_j^{\hat{a} - \hat{c}},$$

(10)

where $S^b$ and $S^{\hat{a} \pm \hat{c}} = (S^{\hat{a}} \pm S^{\hat{c}})/\sqrt{2}$ are the spin operators in a set of three orthogonal directions, with $\hat{a}$, $\hat{b}$, $\hat{c}$ being unit vectors along the orthorhombic crystallographic axes. Here we label each bond $\langle ij \rangle$ by the axis perpendicular to its Ir-O$_2$-Ir plane; for each bond, this normal vector lies along one of the directions $\{(\hat{a} + \hat{c}), (\hat{a} - \hat{c}), \hat{b}\}$. The $\hat{b}_\perp$ bonds are all oriented along the crystallographic $c$ direction. Thus all the nearest neighbor Ir-Ir bonds can be divided into three classes, one for each component of spin: the $\hat{b}$ component from the $c$-axis bonds, and the $\hat{a} \pm \hat{c}$ components from the $h$ bonds defining each honeycomb plane (depicted in red and blue with corresponding $\pm$ signs in Figure 4A of the main text). The exchange couplings $K^h$ are constrained by the symmetry of the space group to be the same on the $(\hat{a} \pm \hat{c})_\perp$ bonds, but $K^c$, the coefficient of $S^b$ coupling, is symmetry-distinct from $K^h$.

The Hamiltonian in Equation 10 was studied by Kitaev on the honeycomb lattice and shown to give an exactly solvable quantum spin liquid. The solution relies on the fact that spin algebra can be represented in an enlarged Hilbert space of Majorana fermions $\chi^\alpha$ ($\alpha = 0, 1, 2, 3$) by mapping $S^\mu \rightarrow (i/2)\chi^0 \chi^\mu$ (where $\mu = 1, 2, 3$) and implementing constraints to project back to the physical Hilbert space. As a result, each spin is represented in terms of two degrees of freedom — one a $\mathbb{Z}_2$ gauge field, the other a Majorana fermion moving in this field. The three-fold local connectivity of the honeycomb lattice together with the orthogonal Ising coupling of the Kitaev Hamiltonian (Equation 10) freezes the gauge field fluctuations associated with the Hilbert space constraint, resulting in static $\mathbb{Z}_2$ fluxes.
problem then reduces to the motion of non-interacting particles in a fixed field. The ground state of these non-interacting fermions, expressed in terms of the underlying spins, is a complicated many-body superposition, and in particular is a quantum spin liquid.

In 2D the solution is possible because the honeycomb lattice contains the right number of hexagon plaquettes (minimal closed paths linking sites) to host the $\mathbb{Z}_2$ fluxes. This can be seen via Euler’s theorem — which states that the number of minimal plaquettes plus the number of sites equals the number of links, on any 2D lattice. Threefold coordination means there are three bonds per two sites, and hence there is one flux degree of freedom for every two spins, as required by the solution. In 3D, there are too many minimal plaquettes to host the required number of independent $\mathbb{Z}_2$ fluxes. However, a similar counting formula shows that the required number of independent gauge field degrees of freedom is matched by subtracting the number of enclosed volumes from the number of faces. Each enclosed volume gives a constraint; the independent flux constraints in 3D are not individual fluxes but rather unending flux lines, which form closed flux loops.

An additional difference in the 3D lattices is that, unlike the 2D honeycomb where every plaquette has six sites, in the harmonic honeycomb lattice the plaquettes vary in length, including 6, 10, 14 and so on. In particular, for the $^9\text{Li}_2\text{IrO}_3$ member there are two minimal plaquettes, 6 sites long and 14 sites long. The product of spin operators around each such plaquette forms an operator which commutes with the Hamiltonian. However products of such plaquette operators around an enclosed volume are reduced to the identity operation, constraining the flux lines to form closed loops. These gauge field fluxes remain static, enabling the spin-liquid solution to be extended to 3D for all members of this family [7, 8].

The ground state of the Hamiltonian described by Eq. 10 contains no gauge-field fluxes. In this zero flux sector, the Hamiltonian is quadratic, diagonal in momentum space. Assuming $K^c = K^h = K$, the dispersion of Majorana Fermions is given by the eight eigenvalues of the
tight-binding matrix

\[
K = \begin{pmatrix}
0 & 1 & 0 & 0 & 0 & 0 & 0 & V_2^* U_3^* \\
1 & 0 & V_1^* & 0 & 0 & 0 & 0 & 0 \\
0 & V_1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & V_1 & 0 & 0 & 0 \\
0 & 0 & 0 & V_1^* & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & V_2^* & 0 \\
0 & 0 & 0 & 0 & V_2 & 0 & 1 & 0 \\
V_2 U_3 & 0 & 0 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}
\]  \quad (11)

where \( U_3 = \exp [i \mathbf{k} \cdot \mathbf{c}] \), \( V_{1,2} = 1 + U_{1,2} \) and \( U_{1,2} = \exp [i \mathbf{k} \cdot (\mathbf{a} \pm \mathbf{b})/2] \) with the \(+/-\) sign corresponding to \( U_1, U_2 \) respectively. In the symmetric octahedra idealization where the Kitaev Hamiltonian is most likely to be relevant, the crystallographic vectors take the simple form \( \mathbf{a} = (2, 2, 0), \mathbf{b} = (0, 0, 4) \) and \( \mathbf{c} = (-6, 6, 0) \) in the Ir-O Euclidean coordinate system, in units where the Ir-O distance is 1. The tight binding dispersion above is easily generalized to the other 3D lattices with the same \( \mathbf{a}, \mathbf{b} \) base-centered orthorhombic Bravais lattice vectors and arbitrarily long unit cells along \( \mathbf{c} \), by appropriately cycling between \( V_1 \) and \( V_2 \) in the alternating off-diagonal elements of the matrix.

The resulting spectrum of the Majorana Fermions is gapless, and remains gapless for the entire region of parameter space with \( K^c \leq 2K^h \) \([7, 8]\). The gapless fermion excitations form a 1D nodal contour within the 3D Brillouin zone, satisfied by the two equations \( \mathbf{k} \cdot \mathbf{c} = 0 \) and \( \cos (\mathbf{k} \cdot \mathbf{a}/2) + \cos (\mathbf{k} \cdot \mathbf{b}/2) = 1/2 \). For reference, note the BZ boundary satisfies the equations \( \cos (\mathbf{k} \cdot \mathbf{c}) = -1 \) or \( \cos (\mathbf{k} \cdot \mathbf{a}/2) + \cos (\mathbf{k} \cdot \mathbf{b}/2) = 0 \).

In the vicinity of the nodal contour the dispersion is linear (\( \omega \sim |\mathbf{k}_{\perp}| \)) in the two directions perpendicular to the nodal contour. Increasing \( K^c/K^h \) shrinks the nodal contour to a point, at \( K^c = 2K^h \); for \( K^c > 2K^h \) the fermion spectrum is gapped.

If flux excitations proliferate, they will confine the fermions excitations in the spin liquid. In 2D, flux excitations are point objects and proliferate at any finite temperature. But in 3D, the fluxes form closed loop, with an energy cost proportional to the length of the flux loop; large flux loop cost arbitrarily high energy. Thus, in the 3D quantum spin liquid the fermions will survive in the deconfined phase until an entropy driven phase transition at finite temperature, separating the 3D quantum spin liquid and the classical paramagnet.
D. Other possible structures

To facilitate our description of the harmonic honeycomb family we develop a simple language based on their structural building blocks. Given a choice of one shared edge, there are two locally indistinguishable choices for the two remaining bonds, shown in Figure 7 (A). Each Ir neighbor can then be in one of two planar environments, which we denote as the harmonic honeycomb plane (Figure 3A of the main text). The vertical (c-axis) bonds can then rotate the orientation of the planes (R-links) or keep them the same (S-links), shown in Figure 7 (B). We emphasize that the Ir is always coordinated by three others in both kinds of bonds, just as in the layered honeycomb. In addition to the harmonic honeycomb family described in the main text, we mention a few other structural possibilities and their consequences here. The main text only describes a family of structures which have \(N\) links of the type \(S\) but only one \(R\) link. We can distinguish members of a more general structural family by different numbers of \(R\) and \(S\) links, and since the stoichiometry is unchanged we denote them \(H\langle N_R, N_S\rangle\)-Li\(_2\)IrO\(_3\). For the \(N_R =\text{odd}\) structures, the crystal structures are orthorhombic. If \(N_R\) is even the material is monoclinic, just as Na\(_2\)IrO\(_3\), which has the \(H\langle 0, \infty \rangle\)-Li\(_2\)IrO\(_3\) structure. Note that even in this case, the \(\sim 70^\circ\) internal bonding geometry is still evident in the angle between the monoclinic crystalline directions \(-a_m\) and \(c_m\). A material containing exclusively \(R\) links, \(H\langle \infty, 0 \rangle\)-Li\(_2\)IrO\(_3\), is the ‘hyper-honeycomb,’ so named in analogy with the hyper-Kagome \cite{7–10}. By changing the number of \(S\) and \(R\) links we can therefore tune the global dimensionality and alternate the symmetry of the materials that are otherwise locally indistinguishable (see Figure 8). Finally, we note that \(S\) and \(R\) links differ in another important regard: \(S\) links are inversion symmetric while \(R\) links are not. For structures containing the latter, this may lead to magnetic components in the Hamiltonian that break inversion symmetry, for example the Dzyaloshinsky-Moriya term \cite{11, 12}. Note this is a local property in that the total space group for the systems may remain inversion symmetric.
IV. SUPPLEMENTARY REFERENCES