Free Standing Large Area Metal-Organic Nanosheets Encapsulating Periodically Spaced Single-Ion Magnets

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Abstract

The high demand for electronic components from limited natural resources is forcing manufacturers to focus on thin-film technology but they are facing problems - limits of operation, uniformity of the films and expensive manufacturing tools. Chemistry can provide solutions to the last two problems with ease of manufacture and uniformity of two-dimensional materials retaining all functionalities within one single layer. Here, we present one such layered compound, $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]_2[\text{Co}^{\text{II}}_2(\mu_2\text{-H}_2\text{O})_3\{\text{Ir}^{\text{III}}(\text{ppy-COO})_3\}_2] \cdot 6\text{H}_2\text{O}$ (**1**). Each charge-balanced layer is an anionic triple-ply holding $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ cations. Treating the crystals with warm acetone or by sonication breaks the weak interlayer supramolecular π - π and H-bonds leading to free standing single- and double layers ($>30 \times 30 \mu\text{m}^2$). Each $\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2$, at crystallographic positions 14.5 Å apart, behaves as a single-ion magnet (SIM). This is the first observation of periodic positioning of SIM shielded from their neighbours amounting to a staggering $350 \times 10^{12} \text{ Co}^{\text{II}}/\text{in}^2$ capable of functioning as a 350 TeraBit/ in^2 magnetic memory device.

Introduction

There are considerable advantages in miniaturisation of electronic components - cost, light weight, energy consumption, increasing the time availability of a limited natural resource, etc..., while also balancing between socio-economic and geopolitical problems.^{1, 2} But there are limiting factors to contemporary materials, in particular those needed for memory devices, due to reliance on collective properties – electricity and magnetism – needing a large ensemble of atoms.³ To overcome these problems manufacturers are tending to materials with properties controlled on a molecule basis – thus, only few atoms.⁴⁻⁶ Present usable materials are built from the bulk, often metals or metal-oxides, and cut to the processable sizes and shapes using high-cost engineering tools and most importantly, there is considerable loss in cuttings. This process is often called top-to-bottom and it is physical. The size of each sensor is limited to *ca.* 25 nm in one direction and the spacing dominated by the width of the cutting tools, often that of the laser beam used in lithography.⁷

Due to the control by chemistry in working from the bottom up, materials made of molecules are challenging the existing extended-solid materials for logical reasons – the device density will be increased, cost will be slashed, life-time of the resources will be extended, etc... – all due to the size reduction to 1 nm or less.⁸ While these are possible using different synthetic chemical processes, it is hampered at the processing stage to organise them in periodic arrays required to ease the device manufacture and usage.⁹

Thus, an in-between method is very appealing and consequently, many researchers have been focusing on materials that can be separated into sheets.^{10, 11} One of the most beautiful examples is the use of the Scotch-tape technique to separate natural graphite down to single layer graphene.¹² This was possible due to the moderate interlayer supramolecular π - π interaction energy. Layered materials have been converted into 2D-sheets by mechanical methods (*e.g.* sonication) and chemical methods through

solvation, functionalisation, etc...¹³⁻¹⁶ On this front there have been considerable developments involving graphene,^{17, 18} graphene oxide,¹⁹ hexagonal boron nitride,²⁰ metal oxides,²¹ metal chalcogenides^{22, 23} and metal hydroxides.²⁴

The major problem of this approach is that the active component for the device is the structure forming unit – for a magnetic memory device it will be the metal ions used as the moment carrier.²⁵ So it still requires to be cut to sizes in excess of a magnetic domain.^{26, 27} That means we still need a cutter and inevitably suffer of loss in cuttings as well as requiring expensive tools. Facing the wall, this is where Chemists appreciate that accident happens and this serendipity leads to a novel material that one can then use to design others. Our work is one of these accidental discoveries while our original aim was focused on photocatalysis, magnetism and luminescence using ordered mixed Ir-Co alloy.^{28, 29}

Here, we present such a case where the choice of the racemic mixture of a metalloligand [Iridium(III)-tris(pyridine-benzoate), Ir(ppy-COOH)₃], a chelating organic agent [terpyridine, terpy] and a paramagnetic transition-metal salt [Co^{II}(ClO₄)₂·6H₂O] from which solvothermal reaction at 100 °C in H₂O-CH₃OH gives red hexagonal crystals of the layered compound, [Co^{II}(terpy)(H₂O)₂@Co^{II}₂(μ₂-H₂O)₃{Ir^{III}(ppy-COO)₃}₂·6H₂O (**1**). Each charge-balanced layer consists of an anionic Ir–Co–Ir triple-ply with cavities accommodating the [Co^{II}(terpy)(H₂O)₂]²⁺ cations and the layers are intercalated by the water molecules providing H-bonds between them in addition to existing π-π ones. When these crystals are treated with warm acetone or by sonication the weak interlayer supramolecular bonds are broken leading to free standing single- and double-layers. The exfoliated 2D-nanosheet (>30×30 μm²) house single-ion magnetic (SIM) cations, Co^{II}(terpy)(H₂O)₂, at crystallographic positions of 14.5 Å apart. This is the first observation of regular periodic positioning of SIM shielded to their neighbours amounting to 350×10¹² Co^{II}/in² or a potential 350 TeraBit/in² magnetic memory device. We propose further where it can lead to with some suggestions.

Results And Discussion

Syntheses and crystal structures. The structure can be broken down to its components to allow us, with additional chemical knowledge, to understand the solvothermal reaction leading to the formation of the compound. From a chemical reactivity point of view the meridian terpy is the most potent chelate and is expected to form first; thus, possibly acts as template. The presence of a racemic mixture of D- and L-Ir(ppy-COOH)₃ is strictly required and the water molecules are as important in the formation of the crystal. Several hexagonal single crystals of **1** (Figure S1), suitable for diffraction intensity data collections gave similar lattice parameters and were isostructural. The experimental PXRD patterns of several batches match well with that calculated from the single crystal structure data (Figure S2). There is no indication of any other crystalline material present. The copper(II) analogue (**2**) has been prepared and structurally characterised but the yield has been low to performed all the required measurements (Table S1).

As expected the C_3 -symmetry of $\text{Ir}(\text{ppy-COOH})_3$ is imposed on **1** which adopts trigonal $P\bar{3}1c$ space-group with an asymmetric unit consisting of $1/3 [\text{Ir}(\text{ppy-COO})_3]^{3-}$, $1/3 \text{Co1}$, $1/6$ terpyridine, $1/6 \text{Co2}$, $5/6$ a coordinate water and one water of crystallisation (Table S1). The key feature of the structure is the rarely seen triple-ply anionic layers $\{[\text{Ir}^{\text{III}}(\text{ppy-COO})_3] - \text{Co}^{\text{II}}_2(\text{H}_2\text{O})_3 - [\text{Ir}^{\text{III}}(\text{ppy-COO})_3]_2\}^{2-}$ having periodic cavities occupied by $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ cations (Figure 1). The anionic layer consists of triangular array of inorganic dimers of face-sharing Co1 , $\{(\text{COO})_3\text{Co}(\mu_2\text{-H}_2\text{O})_3\text{Co}(\text{COO})_3\}^{2-}$, bridged by the tripodal organometallic as ligand leading to the triple-ply arrangement (Figure S3).²⁸ The layer can be considered as consisting of corner-shared triangular biprisms which is different to that of CdI_2 or Brucite which is formed of corner-shared triangular prisms.

The organometallic iridium centres adopt distorted-octahedral geometries [Ir-C : 1.998, Ir-N : 2.118 Å] (Table S2), similar to those reported in other heterometallic Ir-M coordination polymers.³⁰ Each Co1 is coordinated by six oxygen atoms; three from carboxylate and three from water at fairly extended Co-O distances of 2.26 and 2.47 Å, respectively. They are heavily distorted, where the Jahn-Teller axis coincides with the C_3 of the trigonal symmetry cell, and manifested as an open umbrella for the three carboxylates (O-Co-O of 101.2°) but a close one with the bridging water (O-Co-O of 71.8°) (Figure S4). The $\text{Co}\cdots\text{Co}$ distance within the dimer is 3.64 Å. The dimer is involved in a set of strong H-bonds between the non-bonded carboxylate oxygen and that of the bridging water, $\text{O}\cdots\text{OH}_2$ distance of 2.61 Å and $\text{O}\cdots(\text{H}_2\text{O})\cdots\text{O}$ angle of 128.1° . It exerts a considerable influence on the geometry of the carboxylate where the O-C-O angle is widened to 125.4° (Figure S4).

Figure 1. Proposed assembly from molecular building units to crystal of 1 starting from the three components and forming single sheets of trapped cations within hollowed anionic layers that are held together through π - π and H-bond interactions between adjacent layers.

The $[\text{Ir}(\text{ppy-COO})_3]^{3-}$ organometallic ligands are arranged on opposite sides of the anionic layer where one enantiomer with one polarity takes one face the other enantiomer with the opposite polarity on the other face (Figure 1). The resulting layer is neither chiral nor polar and a centrosymmetric cell is formed. Due to the crystal symmetry the carboxylate is coplanar with the phenylpyridine moiety. More interesting is that the cations sitting within the cavities of the layers are crystallographically disordered over three symmetry-equivalent positions. Therefore, it looks like a three-blade propeller with one unit consisting of one Co2 , one terpy and two water molecules (Figure S5). While Co2 is located at a special position with the five sites occupied by three nitrogen atoms as meridian and two water molecules (Co-N , 1.76 - 1.81 Å; Co-O , 2.56 Å). The unique geometry of $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ cations compared to other previously reported pentagonal compounds can be attributed to high symmetry and limited space.³¹ Each cavity houses one unit in a triangular array at a centre-to-centre distance of the crystallography a -axis of 14.5 Å (Figure 1). The $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ cations have no direct chemical bond with the layers, and are only locked in position by two weak $\text{C}\cdots\text{O}$ (pyridine to carboxylate) H-bonds of 3.12 (C14-H14 $\cdots$ O1) and 3.35 Å (C15-H15 $\cdots$ O1). Because each anionic layer consists of edge-sharing bipyramids, it has apices and troughs

and for efficient packing the apices of adjacent layers are translated in the *ab*-plane to fit in the troughs of the centre one (Figure S6). Consequently, the structure adopts an ABABA sequence with two layers per unit cell along the *c*-axis. The layers are locked to each other via a bond-over-ring π - π interaction between adjacent phenyl groups, characterized by C $\cdots$ C distance as short as 3.48 Å (Figure S7). A similar picture to graphite though limited in numbers. The remaining space between the layers is occupied by an octahedron of water molecules with a short (3.09 Å) and a long (3.37 Å) contacts. They form two carboxylate O $\cdots$ O contacts (3.61 and 3.64 Å) and one with the phenyl C $\cdots$ O (3.56 Å).

The chemistry of 2D-materials is dominated by two families; those consisting of neutral or charged layers.³² For both families, solvents can be intercalated or exchanged. It all depends on the balance of electrostatic energies of the host and the intercalant. Additionally, the layer is also amenable to doping with metal-cations or metal-complexes or halogen anions to tune their electronic properties. For example ionic layered materials, such as 2D metal-oxalate network, the compensating charged ions between the sheets can be exchanged by functional ones.^{33,34} Consequently, there is only one 2D material reported that has charge-compensated cations in cavities within its two-dimensional network, and thus allowing free standing neutral monolayer.³⁵ As mentioned by the authors, this type of network can be easily exfoliated into atomically-thin layers by using the Scotch tape method. Since our compound is the second one, as well as being the first with magnetic cation, this report prompted us to explore the production of **1** monolayer with a periodic array of a potential SIM.

Figure 2. From crystal to nanosheets. (a) Microscope photograph of a as-synthesised crystal to (b) an electron-microscope photograph to (c) an AFM photograph of double nanosheet. (d) Structure of one sheet and (e) Tyndall scattering from suspensions of nanosheets obtained by three methods.

Following literature reported techniques, we first used ultrasonic treatment which operates by local microscopic high-temperature heating to break up the layered structure and produce single- or few aggregated-sheets.^{36,37} The successful exfoliation was demonstrated by the observation of Tyndall effect of a laser pointer through acetone suspension (Figure 2) over long periods. Indeed, the uniform sheet morphology of **1** is supported by a SEM and TEM images (Figures 3a-3b, S8). Atomic force microscopy (AFM) images reveal that the sheets are quite uniform with a lateral dimension up to 1.5 μm and thickness of 2.5 ± 0.2 nm (Figure S9), which is equivalent to that of a monolayer (2.2 nm) in the single crystal. However, conventional ultrasonic exfoliation damages the planar structure of the sheets and results in large amount of fragmentation with a lateral dimension of less than 2 μm or riddled with holes. So, it is difficult to produce sheets for making devices. To address these problems, soft-physical processes, such as freeze-thaw method³⁸ and solvent-induced delamination,^{39,40} was used to prepare tens of micron-scale sheets. The latter gives the most uniform, complete and large area single- and double-sheets.

Figure 3. Morphological characterisation of 1. (a) SEM image of the sheets. (b) TEM image of the sheets. AFM image of the sheets prepare by (c) freeze-thaw (20 cycles), (d) freeze-thaw (90 cycles) and (e) the corresponding 3D AFM image. (f) AFM image of the sheets prepare by delamination in acetone.

AFM analyses on samples of different sizes range from freeze-thaw method using acetone as supporting solvent suggest different distributions of multilayers segments where the majority consists of double-layer (3.7 ± 0.2 nm, experimental thickness is 3.5 nm, Figure S11). We hypothesize that the penetration of acetone between the layers impose different constraints on the structure leading to a preferential exfoliation of the crystal into double-sheets. The challenge to exfoliate bulk samples into a single layer structure by this soft physical method remains a real challenge to understand given the balance of external forces versus that of the intrinsic π - π and H-bonding interactions between the sheets. Unlike ultrasonic exfoliation to lateral sizes of 2 μ m, sheets of up to 30 μ m can be obtained by this non-mechanical method (Figure S11). By increasing the number of cycles, further exfoliation follows to bilayers and eventually monolayers (Figures 3c and S12). A homogeneous single-layer state is achieved after 90 repetitions, but at a cost of reducing the lateral dimensions (Figures 3d and 3e).

Going to the softest non-mechanical method where the crystals (average lateral size of 200 μ m) were suspended in acetone and applying a gentle heat to 35 °C for few days and we found the Tyndall effect is enhanced with time. AFM shows principally double-layer segments with very clean surfaces extended over 30 μ m (Figures 3f and S13). The quantity of single-layer sheets is low and this can be increased by shaking the suspension using a vibrating-mixer with little damage to the double-layer segments. The high-quality double-layer sheet obtained by self-delamination has rarely been reported.⁴¹

The PXRD pattern of the as-synthesised crystals shows the Bragg reflections expected from the crystal structure data. No other reflection was observed suggesting the crystals were the only diffracting material and the 2D material maintains good stability during the exfoliation process (Figure 4). Interestingly, the PXRD pattern of the exfoliated sample displays dominant reflections at $2\theta = 6.26, 12.47$ and 18.66° which are assigned to the (002), (004) and (006) reflections, suggesting high preferential orientation which can only be from the re-structuration upon drying. From the width of the Bragg reflections, we can assume the ordering is long-range after re-structuration. Moreover, the morphology and the multilayer crystalline structure are retained in the residual particles formed during the preparation of **1-NS** by different methods (Figure S14-S18).

Figure 4. PXRD patterns for 1: Simulated from single crystal structure data (black), observed for powder of as-synthesized crystals (red) and the drop-cast of exfoliated sheets (blue). The green ticks locate the positions of the Bragg reflections.

Magnetic properties

The temperature dependence of the magnetic moment is presented as the product of susceptibility and temperature ($c_M T$) in figure 5a. The data can be discussed as being composed of three parts and since the two different cobalt atoms are quite far apart and not connected through bonds we can consider the total moment as being the sum from these two parts. On lowering the temperature from 300 to 150 K a gradual drop of the magnetic moment from 0.82 to 0.42 cm³ K/mol is observed. This part is associated to the face-sharing Co₂(μ_2 -OH₂)₃ dimer, that is Co1, which is appropriate for very strong antiferromagnetic

exchange through the three oxygen atoms of the water molecules. Consequently, the value of $0.82 \text{ cm}^3 \text{ K/mol}$ at 300 K is only one tenth of *ca.* $7.5 \text{ cm}^3 \text{ K/mol}$ expected.

The second part, a constant plateau at *ca.* $0.4 \text{ cm}^3 \text{ K/mol}$, is valued to an anisotropic $S = \frac{1}{2}$ moment carrier. We associated this part to the $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ and assume from known examples in the literature that this five-coordinated cation stabilises in the Kramers $S = \pm \frac{1}{2}$ state due to a very strong axial anisotropy (D).³¹ This is projected in the observation of EPR signals starting *ca.* 100 K and increasing in intensity down to 5 K, as well as fitting quite well to an anisotropic g -tensor of low-spin Co^{II} where simulation gives $g_x = 2.208(2)$, $g_y = 2.132(2)$, and $g_z = 2.017(2)$ (Figure 5b).⁴²

Figure 5. Magnetic properties of 1: Temperature dependence of c_M and $c_M T$ measured for a polycrystalline sample under an applied dc-field of 1 kOe, and (b) HF-EPR spectra of a powder sample at a frequency of 120 GHz.

The third part is concerned with the increase below 50 K. Its gradual rise to a peak corresponds to a magnetic long-range ordering (LRO) of an impurity, whose quantity is very small (see below) considering the value of $0.8 \text{ cm}^3 \text{ K/mol}$ at the peak. The LRO is further characterized by bifurcation in the ZFC-FC magnetisation in a field of 10 Oe and the presence of both ac-susceptibility components independent on frequency (Figure S20). EPR spectroscopy shows a broad signal for all frequencies at 300 K at $g = 2.082(2)$ (Figure S21). Its width originating from magnetic coupling and weak dependence of temperature are consistent with a strongly coupled magnetic impurity.

Although the crystals appear very clean under the microscope and by PXRD, the magnetic properties suggest a small amount of a highly magnetic material is present. As mentioned in the synthetic section, a green coloured powder appeared before the reaction mixture was subjected to solvothermal reaction. The high pH condition of the reaction should be the reason which may lead to magnetic layered hydroxide specially in the presence of an organic carboxylate.⁴³ The green colour of the particles is known to originate from structures containing both octahedral and tetrahedral coordinated cobaltous ions.⁴⁴ Surprisingly, both SEM and PXRD measurements do not show two phases. The magnetic properties of the green powder, isolated before the solvothermal treatment, exhibit long-range-ordering characteristics of the ferrimagnetic material and also confirms the above hypothesis (Figure S22). Comparison of the moment in **1** to those of two samples of the green impurity those of collected before hydrothermal treatment gives an estimate of less than 1/500 in weight.

Furthermore, ac-susceptibility measurements in applied fields suggest an underlying moment displaying slow magnetic relaxation (Figure S23). As the dimer will be silent at low temperatures due to it being in the $S = 0$ ground-state and the magnetic impurity will be fully saturated in a field of 3 kOe, the only varying ac-susceptibility can only originate from superparamagnetism (Figure 6a). This can only come from $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ within the cavities. We believe their segregation within each layer diminish any exchange between nearest neighbours so that the frequency dependence can be observed. The presence

of both ac-susceptibility components are exacerbated by the Cole-Cole behaviour when plotted in an Argand diagram (Figure 6b). This behaviour persists up to 8 K and analyses of the temperature dependence data using standard procedure gave a barrier to magnetisation reversal of 28 K and a relaxation time of 3.72×10^{-5} s (Figure S24). If one consider that each $[\text{Co}^{\text{II}}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ is behaving as a memory site within the layer, this particular free-standing layer is one with the highest ever density known. A calculation using the crystallographic dimension of 14.5 Å spacing gives a staggering 350×10^{12} $\text{Co}^{\text{II}}/\text{in}^2$, translating to a potential 350 TeraBit/ in^2 magnetic memory device. All the more important, the ac-susceptibility of a sample consisting principally of double layers would also exhibit similar results (Figures 6c, 6d and S25).

Figure 6. Magnetisation dynamics from ac-susceptibilities measured in the temperature range 1.8-8.0 K under 3 kOe bias dc field: Frequency dependence of the out-of-phase (c") ac-susceptibility and Cole-Cole plots of **1** (a, c) and **1-NS** (b, d).

Conclusions

In self-assembling paramagnetic cobalt(II) with the metalloligand $[\text{Ir}(\text{ppy-COOH})_3]$ in the presence terpyridine to study the combine luminescence and magnetic properties and catalytic effect of Co-Ir, a unique layered compound is obtained which is easily delaminated to double and single nanosheets. Its uniqueness is in its content, which consists of anionic tri-ply, Ir-Co-Ir, encapsulating the cation $[\text{Co}(\text{terpy})(\text{H}_2\text{O})_2]^{2+}$ within its cavities. Applying three different methods – ultrasonication, freeze-thaw, and soaking in acetone – the layers were separated to nanosheets of lateral dimension exceeding $30 \times 30 \mu\text{m}^2$. Each cation behaves as an independent magnet – single-ion magnet (SIM) – due to the negligible dipolar interaction favoured by their periodic spacing of 14.5 Å apart. Each layer is ordered like bottles in a rack. This amounts to 350 SIM/ in^2 ; each relaxes in a time of 3.72×10^{-5} s. While the density compares to ~ 300 times the currently available maximum density, the technological advances on the read/write head are lagging behind. Assuming a collection of say 5×5 SIM is used per bit it should be possible to theoretically put over ten pocket hard discs on the current market into a matchbox sized device.

Methods

Materials and physical measurements. All starting materials were of reagent grade quality and were obtained from commercial sources without further purification. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K_α) at room temperature. Infrared spectra were measured as KBr pellets on a Bruker Tensor 27 spectrometer in the range of 400 - 4000 cm^{-1} . Thermogravimetric analyses (TGA) were performed under a flow of nitrogen in the temperature range 25 - 600 °C at a heating rate of 5 °C / min using a METTLER TOLEDO TGA/DSC 1 instrument. Elemental analyses for C, H and N were obtained with a Perkin Elmer 240C elemental analyser. Atom force microscope (AFM) measurements were carried out on VEECO Inc Multimode V. Scan electron microscopy (SEM) was performed on SHIMADZU SSX-550. The magnetic data were obtained on

polycrystalline and powder samples using a Quantum Design SQUID VSM system. The diamagnetic contributions of the samples were estimated from Pascal's constants.⁴⁵

Synthesis of [Co^{II}(terpy)(H₂O)₂@Co^{II}₂(H₂O)₃{Ir^{III}(ppy-COO)₃]₂·6H₂O (1). Ir(ppy-COOH)₃ (0.04 mmol, 31.5 mg) was suspended in 12 mL of distilled water and dissolved by adjusting the pH to 12.5 with 6 M aqueous NaOH. Then terpyridine (0.03 mmol, 7 mg) in 0.4 mL MeOH was added followed by 0.08 mmol Co(ClO₄)₂·6H₂O in 4 mL water. An immediate precipitation of a green powder appeared. After keeping the vial at 100 °C for 2 days, red block crystals were obtained. The crystalline product of **1** was separated by filtration and washed with distilled water ten times to completely remove the residual ligand and metal salt. Anal. calcd (%) for C₈₇H₇₅N₉Co₃Ir₂O₂₃: C, 48.02; H, 3.47; N, 5.79. Found: C, 49.33; H, 3.81; N, 6.19. IR data (KBr, cm⁻¹): 3600 (w), 3402 (s), 3066 (w), 1629 (s), 1587 (s), 1560 (s), 1510 (m), 1475 (m), 1450 (m), 1406 (m), 1375 (s), 1315 (m), 1271 (m), 1234 (m), 1056 (w), 1028 (m), 777 (s), 729 (w), 690 (w), 644 (w), 509 (w) (Figure S26). Thermal analysis reveals that the water molecule can be completely removed below 140 °C, corresponding to the release of nine (25 - 80 °C) and two (80 - 140 °C) water molecules (Figure S27). The total weight loss is 9.87 %, in agreement with the removal of six lattice and five coordinated water molecules (calcd. 9.10 %). According to this result, the elemental analysis sample may have lost three water before tested, and the results are consistent with formula C₈₇H₆₉N₉Co₃Ir₂O₂₀ (calcd. (%) C, 49.24; H, 3.28; N, 5.94).

Exfoliation into sheets. For all the exfoliation experiments the following was adopted. Crystals of **1** (2 mg) were suspended in acetone (4 mL) followed by different methods of exfoliation and finally separated from the large particles by centrifugation at 14,000 rpm for 15 minutes and further free-standing the colloidal suspension for at least 2 days before use. Three methods with different degrees of energy for the exfoliation were applied, (a) strong: treatment in an ultrasonic bath (300 W) at room temperature for 3 hours; (b) mild: the crystals in acetone were frozen in a liquid nitrogen bath (-196 °C) until solid followed by immediate heated in a warm water bath (55 °C) for 5 min and repeated for the desired number of times, and (c) soft: keeping in warm acetone at 35 °C for several days leads to low quantity of large double-sheets and using a vibrating mixer increases the quantity. The suspensions of **1-NS** in acetone were deposited by being drop-cast onto mica substrates (20 µL), and carbon-coated copper grids (5 µL) for AFM and TEM measurements, respectively. Considering the efficiency of preparation, the nanosheet samples which prepared by freeze-thaw with 20 cycles were collected for other measurements.

Single-crystal structure determination. Crystals were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 153 K. The data collected on one selected crystal were integrated using the Siemens SAINT program,⁴⁶ with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector face plate. Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.⁴⁷ All of the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically with the isotropic thermal parameters related to the

non-hydrogen atoms to which they are bonded. Crystallographic and refinement details are listed in Table S1.

Data availability

We declare that the data supporting the findings of this study are available within the article and Supplementary Information file or from the corresponding author upon reasonable request.

Declarations

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Author contributions

F.K., M.K. and L.M.Z. conceived and designed this work. F.K. carried out the syntheses and characterizations. S.S.B. solved the X-Ray structure. X.D.H performed the magnetic measurements. X.X.T., Z.X.W. and Z.W.O investigated the EPR properties. F.K., M.K. and L.M.Z. interpreted the results and wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Proposed assembly from molecular building units to crystal of **1** starting from the three components and forming single sheets of trapped cations within hollowed anionic layers that are held together through π - π and H-bond interactions between adjacent layers.

Figure 2

From crystal to nanosheets. (a) Microscope photograph of a as-synthesised crystal to (b) an electron-microscope photograph to (c) an AFM photograph of double nanosheet. (d) Structure of one sheet and (e) Tyndall scattering from suspensions of nanosheets obtained by three methods.

Figure 3

Morphological characterisation of 1. (a) SEM image of the sheets. (b) TEM image of the sheets. AFM image of the sheets prepared by (c) freeze-thaw (20 cycles), (d) freeze-thaw (90 cycles) and (e) the corresponding 3D AFM image. (f) AFM image of the sheets prepared by delamination in acetone.

Figure 4

PXRD patterns for 1: Simulated from single crystal structure data (black), observed for powder of as-synthesized crystals (red) and the drop-cast of exfoliated sheets (blue). The green ticks locate the positions of the Bragg reflections.

Figure 5

Magnetic properties of 1: Temperature dependence of χ and χT measured for a polycrystalline sample under an applied dc-field of 1 kOe, and (b) HF-EPR spectra of a powder sample at a frequency of 120 GHz.

Figure 6

Magnetisation dynamics from ac-susceptibilities measured in the temperature range 1.8-8.0 K under 3 kOe bias dc field: Frequency dependence of the out-of-phase (χ'') ac-susceptibility and Cole-Cole plots of 1 (a, c) and 1-NS (b, d).

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