Magnetic Archimedean Tessellations in Metal-Organic Frameworks

Hua Chen, Laura Voigt, Mariusz Kubus, Dmytro Mihrin, Susanne Mossin, René Wugt Larsen, Søren Kegnæs, Stergios Piligkos, Kasper Pedersen

Submitted date: 03/05/2021 • Posted date: 05/05/2021

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Citation information: Chen, Hua; Voigt, Laura; Kubus, Mariusz; Mihrin, Dmytro; Mossin, Susanne; Larsen, René Wugt; et al. (2021): Magnetic Archimedean Tessellations in Metal-Organic Frameworks. ChemRxiv. Preprint. <https://doi.org/10.26434/chemrxiv.14529090.v1>

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Magnetic Archimedean Tessellations in Metal-Organic Frameworks

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The self-assembly of trivalent lanthanide ions with ditopic organic spacers results in the formation of complex tiling patterns that mimic the structural motifs of quasi-periodic 2D materials. The assembly of $\text{trans-}\{\text{LnI}_2\}^+$ nodes ($\text{Ln} = \text{Gd}, \text{Dy}\})$ with both closed-shell and anion radicals of 4,4'-bipyridine affords rare examples of Archimedean tessellations in a metal-organic framework. We furthermore demonstrate occurrence of sizable magnetic exchange interactions and slow relaxation of magnetization behaviour in a complex tessellation pattern. The implementation of Archimedean tessellations in lanthanide(III) coordination solids couriers a strategy to design elusive quasi-periodic metal-organic frameworks with inimitable magnetic properties.

The design and realization of complex and aperiodic two-dimensional tessellations in molecule-based materials constitutes a novel route to harvest physical properties, for instance photonic, electronic, magnetic, and phononic characteristics, which are expected to be unparalleled compared to their periodic counterparts.^[1–3] However, applications are elusive due to the severe scarcity of materials exhibiting the desired structural motifs. The two-dimensional dodecagonal quasicrystalline phase (Fig. 1a, ddQC) is well-known in both hard and soft materials, as well as in supramolecular networks.^[4–6] Herein, the tessellation of triangles and squares, present in a ratio of $4/\sqrt{3} \approx 2.3$, leads to the disappearance of periodicity and the formation of local 12-fold rotational symmetry. Generally, quasicrystals are found in the vicinity of structurally related, periodic structures and the ddQCs, specifically, often co-occur with the periodic Archimedean tessellations (ATs, Fig. 1bc), which are therefore referred to as quasicrystal approximants.^[7] Interestingly, the sole example of a quasicrystal phase found in a metal-organic network structure was realized in single-atom layers, by co-evaporating large Eu atoms and organic linkers.^[8–10] The construction of five- and six-fold nodes is critical for the realization of such structures and necessitates confining five or six chemical bonds to the plane (cf. Fig. 1a). This requirement precludes the use of most transition metal-ions as nodes but may be met by larger metal ions as those found in the f-block. In the fragile single-layer materials, the exact chemical nature, such as

the oxidation state of the 4f ion nodes, remains unknown. In the more robust, bulk coordination networks and metal-organic frameworks (MOFs), quasicrystals are elusive.^[1] This may partly be related to the complications in their crystallographic identification and partly due to the scarcity of structures that bear the potential to express quasicrystallinity. The elongated triangular ($3^3.4^2$) and snub square ($3^2.4.3.4$) ATs (Fig. 1bc) each possess a triangle-to-square ratio of 2 and have been desired structural motifs in the quest for ddQCs. However, even realizations of MOF structures complying to these ATs are exceedingly scarce.

Figure 1. (a) An example of a random-tiling ddQC, (b) the semiregular elongated triangular tiling, and (c) the semiregular snub square tiling.

Taking advantage of the common pentagonal bipyramidal coordination motif of the uranyl ion, $\text{trans-}\{\text{UO}_2\}^{2+}$, Smetana *et al.* reported the first example of a snub square tiling in a metal-organic bulk material.^[11] We recently reported the utilization of $\text{trans-}\{\text{YbI}_2\}$ nodes as five-vertex building units to form the triangular elongated tiling in $\text{YbI}_2(\text{bipy})_{5/2}$ ($\text{bipy} = 4,4'$ -bipyridine; cf. Fig. 1b).^[12] The lanthanide ions are particularly relevant for the realization of both ATs and ddQC phases as the coordinative plasticity allows for their incorporation in a variety of local coordination geometries. Furthermore, their weak interactions with ligands are commensurable with the weak interactions typically intrinsic to aperiodic structures.^[1] The construction of the $\text{YbI}_2(\text{bipy})_{5/2}$ framework necessitated the introduction of divalent lanthanide units, whose preponderance in chemistry is dwarfed by the trivalent ones. To circumvent this problem, we herein demonstrate a novel strategy to design molecule-based magnetic Archimedean tessellations incorporating trivalent lanthanide ions.

Scheme 1. Synthetic route to Gd and Dy.

The reaction of sodium metal with bipy was early reported to generate the anion radical $\text{bipy}^{\bullet-}$.^[13] However, to date, only a

[*] H. Chen, Dr. L. Voigt, Dr. Mariusz Kubus, Dr. D. Mihin, Prof. Dr. S. Mossin, Prof. Dr. R. W. Larsen, Prof. Dr. S. Kegnæs, Prof. Dr. K. S. Pedersen
Department of Chemistry
Technical University of Denmark
Kemitorvet, Building 207, DK-2800 Kgs. Lyngby, Denmark
E-mail: kastp@kemi.dtu.dk (K.S.P.)
Web: www.kemi.dtu.dk/pedersen

Prof. Dr. S. Piligkos
Department of Chemistry
University of Copenhagen
DK-2100 Copenhagen, Denmark

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/>

single crystalline compound is known to incorporate this chemical species, $\text{Na}^+(\text{en})(\text{bipy}^{\bullet-})$ (en = ethane-1,2-diamine).^[14] The reaction of sodium with an excess of bipy in CH_3CN affords an intensely dark-blue colored solution. The X-band electron paramagnetic resonance (EPR) spectrum of the frozen solution yields a single narrow resonance at $g = 2.00$ (Fig. S1, Supporting Information), compatible with the formation of an organic radical and similar to that of $\text{Na}^+(\text{en})(\text{bipy}^{\bullet-})$ ($g = 2.00429$).^[14] The addition of solid GdI_3 to the $\text{bipy}^{\bullet-}/\text{bipy}$ solution results in an immediate formation of a dark-blue microcrystalline powder which exhibits a broad EPR signal (Fig. S2, Supporting Information). The elemental analyses of C, H, N, Gd, I, and Na indicate a formulation of $\text{GdI}_2(\text{bipy})_{5/2} \cdot \text{CH}_3\text{CN}$ and no presence of Na^+ (cf. Supporting Information). Careful layering of the dark-blue $\text{bipy}^{\bullet-}/\text{bipy}$ solution onto CH_3CN -covered solid GdI_3 affords block-like, dark-blue crystals of **Gd** suitable for single-crystal X-ray diffraction. **Gd** crystallizes in the tetragonal $I4_122$ space group and features an ideal snub square tessellation of $\text{GdI}_2(\text{bipy})_{5/2} \cdot x\text{CH}_3\text{CN}$ (cf. Fig. 2a).

Figure 2. (a) Single-crystal X-ray structure of **Gd** viewed perpendicular to one of the snub square tiling layers. (b) Single-crystal structure of the trace impurity phase **Gd'**. Color codes: Gd, turquoise; I, purple; N, blue; C, grey. H atoms and co-crystallized CH_3CN molecules have been omitted for clarity.

The coordination geometries of the two crystallographically independent Gd centers are almost identical. The Gd—I bond lengths of 3.0437(7)–3.054(2) Å are slightly longer than those found in *trans*- $[\text{Gd}^{\text{III}}\text{I}_2(\text{thf})_5]^+$ (thf = tetrahydrofuran) of 3.00 Å,^[15] albeit significantly shorter than the Eu—I bonds found in *trans*- $[\text{Eu}^{\text{III}}\text{I}_2(\text{thf})_5]$ of 3.22–3.24 Å,^[16] corroborating the presence of Gd(III), and not the extremely rare Gd(II), in **Gd**.^[17] The N—Gd—N angles are in the range of 68.1(2)° to 75.3(3)° and together with the I—Gd—I linearity (179.23(4)°, 177.90(5)°) reflect the close proximity of the local coordination environment to D_{5h} symmetry. The presence of Gd(III) necessitates one $\text{bipy}^{\bullet-}$ radical ligand per $\text{GdI}_2(\text{bipy})_{5/2}$ formula unit. Goicoechea and coworkers have previously shown that the inter-pyridinic bond in bipy shortens by ~4% upon one-electron reduction.^[14] According to that, in **Gd**, the two crystallographically independent Gd centres are each surrounded by three $\text{bipy}^{0/\bullet-}$ ligands with longer C—C bond lengths of 1.49(3)–1.51(2) Å and two $\text{bipy}^{0/\bullet-}$ ligands with short C—C bond lengths of 1.45(2) Å corresponding to a reduction of ~4%. Interestingly, the anticipated localized $\text{bipy}^{\bullet-}$ ligands span the edges of the triangles in only one direction of the plane which leads to the formation of $\{\text{Gd}^{\text{III}}_4(\text{bipy}^{\bullet-})_4\}$ rhombi (Fig. S3). The presence of mixed valency in the $\text{bipy}^{0/\bullet-}$ scaffold could be expected to lead to strong inter-valence charge transfer (IVCT) transitions in the mid- or near-infrared spectrum as e.g. observed in transition metal complexes of mixed-valent 2,2'-bipyridine^{0/•-}.^[18] However, no such IVCT bands could be observed in **Gd** (Fig. S6, Supporting Information) which may, tentatively, be attributed to the weakly covalent nature of metal-ligand bonds and the localization of the unpaired electron, as inferred from crystallography. Notably, in each crystallization vial, a few needle-shaped dark-blue crystals of **Gd'** were systematically obtained. The structural analysis of **Gd'** revealed an identical chemical composition of $\text{GdI}_2(\text{bipy})_{5/2} \cdot x\text{CH}_3\text{CN}$, but **Gd'** crystallizes in the triclinic $P\bar{1}$ space group and resembles an elongated triangular tiling similar to the previously reported $\text{YbI}_2(\text{bipy})_{5/2}$ structure (Fig. 2b). However, in contrary to $\text{YbI}_2(\text{bipy})_{5/2}$, the tilting angle, α (cf. Fig. 1b), departs significantly from 90° and amounts to 101°. Thus, the Gd centres could, as well, be considered as approaching defect 6-fold nodes, corresponding to $\alpha = 120^\circ$. Similarly to **Gd**, two fifths of the bipy display short inter-pyridinic C—C bonds of an average length of 1.44(2) Å and three fifths exhibit normal, longer C—C bonds of 1.51(1)–1.53(2) Å, echoing the existence of Gd(III) and both bipy and $\text{bipy}^{\bullet-}$ in **Gd'**. Use of DyI_3 reveals an identical behavior and yields $\text{DyI}_2(\text{bipy})_{5/2} \cdot x\text{CH}_3\text{CN}$ (**Dy**). **Dy** is isostructural to **Gd** with slightly contracted bond lengths. Notably, no traces of an elongated triangular tessellation phase could be observed for Dy.

The room temperature value of the magnetic susceptibility-temperature product, χT , of **Gd** amounts to 8.6 cm³ K mol⁻¹, close to the value expected for an uncorrelated pair of a Gd(III) ion (4f⁷) and an organic radical ($S = 1/2$, $g = 2.0$) of 8.3 cm³ K mol⁻¹. The χT product decreases only slightly by cooling reflecting the relatively weak Gd^{III}- $\text{bipy}^{\bullet-}$ superexchange interactions. Similarly, the field-dependence of the magnetization, M vs H , reveals that M saturates at low temperature at 8.0 μ_B , as expected for one Gd^{III} and one $\text{bipy}^{\bullet-}$ per formula unit, only weakly magnetically coupled. The structural analyses suggested the presence of $\{\text{Gd}^{\text{III}}_4(\text{bipy}^{\bullet-})_4\}$

Figure 3. Temperature dependence of the magnetic susceptibility-temperature product, χT , for polycrystalline **Gd** and **Dy** obtained under a dc magnetic field of $\mu_0 H = 1000$ Oe. The solid black line is the best fit as described in the main text. The insets show the magnetic-field dependence of the magnetization, M , plotted against $\mu_0 H T^{-1}$.

rhombi. Herein, the adjacent Gd^{III} and $\text{bipy}^{\bullet-}$ are expected to be coupled by the superexchange mechanism. Thus, the magnetization data were modelled using a spin-Hamiltonian (Eq. 1) for an eight-membered ring of alternating $\text{Gd}(\text{III})$ ions and $\text{bipy}^{\bullet-}$ radicals:

$$\hat{H} = g\mu_B\mu_0 H \sum_i \hat{S}_i + J (\hat{S}_{\text{Gd1}}\hat{S}_{\text{rad1}} + \hat{S}_{\text{Gd2}}\hat{S}_{\text{rad1}} + \hat{S}_{\text{Gd2}}\hat{S}_{\text{rad2}} + \hat{S}_{\text{Gd3}}\hat{S}_{\text{rad2}} + \hat{S}_{\text{Gd3}}\hat{S}_{\text{rad3}} + \hat{S}_{\text{Gd4}}\hat{S}_{\text{rad3}} + \hat{S}_{\text{Gd4}}\hat{S}_{\text{rad4}} + \hat{S}_{\text{Gd1}}\hat{S}_{\text{rad4}}) \quad (\text{Eq. 1})$$

where $g = 2$ is the isotropic g factor for both Gd^{III} and the radical spins, μ_B is the Bohr magneton, H is the magnetic field, $\hat{S}$ is a spin operator indexed appropriately for each Gd^{III} and $\text{bipy}^{\bullet-}$, and J is the coupling constant. The first term represents the Zeeman interaction for all Gd^{III} and radical spins and the second term accounts for the superexchange interaction. Anisotropy terms are neglected since they are expected to be small for Gd^{III} and for the $\text{bipy}^{\bullet-}$ radical. The dimension of the matrix representation of Eq. 1 for **Gd** is 65536, which is impractical with respect to standard numerical full matrix diagonalization approaches. Thus, for the quantitative interpretation of the magnetic properties of **Gd**, we used home-written software (ITO-MAGFIT)^[19] that makes use of irreducible tensor operator algebra^[20] to block-diagonalize the spin-Hamiltonian and the Levenberg–Marquardt algorithm^[21] to fit the magnetization data. The χT product and the M vs H data of **Gd** were simultaneously fitted to spin-Hamiltonian (Eq. 1). This resulted to the best fit superexchange coupling constant $J/hc = 0.073(4) \text{ cm}^{-1}$ (Fig. 3, black trace, and Fig. S7, Supporting Information). Under these conditions, the spin ground state of **Gd** is an $S = 12$ (Fig. S8, Supporting Information), separated from the first excited state, a degenerate doublet of $S = 11$ states, by only 0.16 cm^{-1} at zero magnetic field. This vanishing value of J is noteworthy although not uncommon for $\text{Gd}(\text{III})$ -radical complexes.^[22] For **Dy**, the room temperature χT product leans at $13.8 \text{ cm}^3 \text{ K mol}^{-1}$, which is only slightly lower than the expected value for a Dy^{3+} ion with a $^6\text{H}_{15/2}$ ground term ($C = 14.2 \text{ cm}^3 \text{ K mol}^{-1}$) and a $\text{bipy}^{\bullet-}$ ligand. The χT product decreases slightly at

Figure 4. M vs $\mu_0 H$ data obtained at $T = 2.1 \text{ K}$ (sweeping rate of 200 Oe s^{-1}) and the first derivative, $dM/d(\mu_0 H)$.

lower temperatures due to depopulation of excited ligand field states. Below *ca.* 15 K, the χT product drops abruptly, which may be ascribed to magnetic superexchange interactions. The M vs H data (Fig. 3 (inset), Fig. 4) reveal a clear step at *ca.* 3 T. Notably, a similar step feature was previously observed in a $\text{Dy}(\text{III})$ -radical chain system, but absent in the isostructural $\text{Gd}(\text{III})$ system, and attributed to the presence of significant exchange interactions in the $\text{Dy}(\text{III})$ system.^[23,24] At fields smaller than $\sim 3 \text{ T}$, the M vs H data show the opening of a small hysteresis gap that collapses again when zero field is approached (Fig. 4). Several Dy^{3+} complexes with approximate local D_{5h} symmetry have been shown to exhibit exceedingly large energy barriers to magnetization reversal exceeding 1000 cm^{-1} .^[25–27] Furthermore, engendering metal ion-radical pairs has proven successful to substantially increase the coercivity and operation temperatures of magnetic materials.^[28–32] Alternating current (ac)

Figure 5. In-phase (χ' , left) and out-of-phase (χ'' , right) ac susceptibility data for polycrystalline **Dy** obtained at selected temperatures and in the absence of a static (dc) magnetic field. Inset: temperature dependence of the paramagnetic relaxation rate, τ^{-1} , vs the reciprocal temperature. The solid lines are simulations as described in the main text.

susceptibility measurements of **Dy** reveal the existence of slow relaxation of magnetization in the absence of a dc magnetic field (Fig. 5). The temperature of the spin-lattice relaxation rate, approximated from the maxima of the $\chi''(\nu_{ac})$ as $\tau^{-1} = 2\pi \nu_{ac}$ (Fig. 5), was modelled a sum of a term governing the temperature independent quantum tunneling of the magnetization (QTM) and a term representing the two-phonon Orbach process, that is often invoked to rationalize the relaxation in lanthanide-based single-molecule magnets:

$$\tau(T)^{-1} = \tau_{\text{QTM}}^{-1} + \tau_0^{-1} e^{-\Delta/k_B T} \quad (\text{Eq. 2})$$

The τ vs T data are well described by $\tau_{\text{QTM}} = 0.4 \mu\text{s}$ and $\Delta/hc = 22 \text{ cm}^{-1}$ ($\tau_0^{-1} = 1.2 \times 10^{-7} \text{ s}$; Fig. 5, green trace). This value of Δ is dwarfed by those of other D_{5h} symmetric SMMs, however, these systems all display the presence of strongly ligand-field perturbing ligands in the axial positions, which contrasts the weakly coordinating iodide ligands in **Dy**. The application of a sizable, static dc magnetic field of 3 T breaks the tunneling pathway (Figs S9–11, Supporting Information) and the τ vs T data can be modelled by the inclusion of the Orbach process only ($\Delta/hc = 63 \text{ cm}^{-1}$ and $\tau_0^{-1} = 3.5 \times 10^{-10} \text{ s}$; Fig. 5, red trace).

The isolation of ddQCs and Archimedean tessellations of lanthanide metal-organic networks on metallic surfaces was attributed to significant interactions with the substrate that enforces planarization of the material.^[10] Indeed, the equatorial linking of the kinetically labile *trans*- $\{\text{M}_2\}^+$ units may be considered as an analogue of the theoretical scenario of soft, isotropic particles moving in 2D, that has been utilized to explain the formation of ddQCs.^[33,34] Herein, we have demonstrated the possibility to construct chemically well-defined Archimedean tessellations of the trivalent lanthanide ions in MOF structures as exemplified by **Gd**, **Gd'**, and **Dy**. The tweaking of these systems towards their quasicrystalline variants necessitates the inclusion of local 6-fold (D_{6h} symmetric) nodes (cf. Fig. 1a), which, despite the large ionic radii, are uncommon for lanthanide complexes.^[35] The structure of **Gd'** is remarkable as it gives a prospect on how to introduce the triangle-rich regular triangular motif without the highly uncommon coordination of six ligands in the equatorial plane, necessary to form ddQCs. Whilst previous reports have shown the viability of lanthanide atoms to act as nodes in surface-confined ATs and ddQC, the strategy presented herein constitutes the first generalizable approach to bulk MOF materials possessing both periodic, aperiodic and fractal geometries.

Acknowledgements

K.S.P. thanks the VILLUM Foundation for a VILLUM Young Investigator grant (15374), the Carlsberg Foundation for a research infrastructure grant (CF-17-0637), the Independent Research Fund Denmark for a Sapere Aude: DFF-Starting Grant, the Danish Society of the Dissemination of Science for a Kirstine Meyer's Memorial Award. H.C., S.K., and K.S.P. thank the Danish National Committee for Research Infrastructure for funding (ESS Lighthouse "SMART").

Conflict of interest

The authors declare no conflict of interest.

Keywords: lanthanides • single-molecule magnets • metal-organic frameworks • quasicrystal approximants

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Supporting Information

Magnetic Archimedean Tessellations in Metal-Organic Frameworks

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Larsen, Søren Kegnæs, Stergios Piligkos, Kasper S. Pedersen

Materials and Methods

All procedures were carried out in an InertLab glovebox under a dry Ar atmosphere. Elemental analysis was performed by the Mikroanalytisches Laboratorium Kolbe (Oberhausen, Germany). GdI_3 (99.99%) and DyI_3 (99.99%) were supplied by Alfa Aesar, and sodium and 4,4'-bipyridine (bipy; 98%) were supplied by Sigma-Aldrich. All reagents were used as received. Dry and oxygen-free solvents were obtained from a Puresolv MD 7 solvent purification system.

Synthesis

Gd: Powdered GdI_3 (135 mg, 250 μmol) and acetonitrile (14 mL) were stirred vigorously for 30 min. An acetonitrile solution (7 mL) of 4,4'-bipyridine (195 mg, 1.25 mmol) and sodium metal (5.8 mg, 250 μmol) was added dropwise to the GdI_3 suspension with stirring. A dark blue microcrystalline powder formed immediately. The mixture was left stirring for 10 min. The solid material isolated by suction filtration and washed with cold acetonitrile ($-20\text{ }^\circ\text{C}$; $2 \times 10\text{ mL}$). Yield: 90 mg (45%). Anal. calcd. (found) for $\text{C}_{27}\text{H}_{23}\text{GdI}_2\text{N}_6$ (corresponding to $\text{GdI}_2(\text{bipy})_{5/2} \cdot \text{CH}_3\text{CN}$): C, 38.5 (38.2); H, 2.73 (2.81); N, 9.98 (9.91); I, 30.2 (29.7); Gd, 18.7 (18.3). Dark-blue single-crystals suitable for single-crystal X-ray diffractometry were obtained by slow diffusion of the two solutions over several days. **Gd'** formed as a trace byproduct phase.

Dy: The synthesis of **Dy** is identical to that of **Gd** but employs DyI_3 . Single-crystals of **Dy** are grown similarly to **Gd**. Yield: 86 mg (43%). Anal. calcd. (found) for $\text{C}_{27}\text{H}_{23}\text{DyI}_2\text{N}_6$ (corresponding to $\text{DyI}_2(\text{bipy})_{5/2} \cdot \text{CH}_3\text{CN}$): C, 38.2 (38.1); H, 2.73 (2.76); N, 9.91 (9.87); I, 29.9 (29.9); Dy, 19.2 (19.3).

EPR spectroscopy

EPR spectra of both solid samples and frozen solutions were obtained at 77 K on a Bruker EMX X-band EPR spectrometer (rectangular cavity ST4102) fitted with a small dewar for liquid nitrogen. The experimental parameters for the frozen solution of a freshly made solution of $\text{Na}^+(\text{bipy}^{\bullet-})$ were: Microwave frequency 9.52 GHz, power 0.42 mW, time constant 20 ms, field interval 338.5-340.5 mT, modulation frequency 100 kHz, amplitude 1.0 G. The observed line is very intense and narrow and can be simulated with a g -value of 2.0045 and a lorentzian lineshape (line width 0.15 mT). After addition of GdI_3 to the solution the precipitated solid were extracted and washed. The EPR signal of the solid is very broad and spans the field interval from 0-0.65 T. The parameters used for the solid sample were microwave frequency 9.52 GHz, power 6.6 mW,

time constant 20 ms, field interval 42-642 mT, modulation frequency 100 kHz, amplitude 5 G. A small signal at $g = 2$ is seen in the spectrum, Fig. S2. This is due to an exceedingly tiny amount of the radical precursor.

X-ray diffraction

Single-crystals of **Gd**, **Gd'**, and **Dy** were immersed in polybutene oil (Aldrich, >90%) and mounted on a nylon loop, which was attached to a SuperNova Dual Source CCD-diffractometer. Data were collected using Cu K α ($\lambda = 1.5406$ Å) radiation at 100(1) or 120(1) K. The structures were solved in Olex2¹ using the structure solution program olex2.solve 1.3² for **Gd**, **Dy**, and SHELXT 2018/2³ for **Gd'** and subsequently refined with the SHELXL⁴ refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically. For both **Gd** and **Dy** the structure was refined as an inversion twin with a BASF parameter of 0.501(7). Due to bipy disorder, it was necessary to enforce ISOR restraints on the ADPs for the C24 and N2 atoms. The distance DFIX restraints were used for the bipy molecule with the N6 atom. The geometry of the acetonitrile molecules was restrained using the DFIX, SIMU, and RIGU instruction (molecules imported from FragmentDB^{5,6} [1, 2]). Additionally, ADPs of C28, C41, and all atoms in the acetonitrile molecules with N9, N10, N11, N12, N14, N15 were restrained to behave isotropically (ISOR). The powder X-ray diffraction patterns were collected using Cu K α ($\lambda = 1.54056$ Å) radiation in the range $6^\circ < 2\theta < 32^\circ$, with a 2θ step size of 0.01° using the SuperNova Dual Source CCD diffractometer. The diffraction pattern of **Dy** was collected at 296 K with an exposure time of 10 minutes. The XRD pattern of **Gd** was collected at 295 K with an exposure time of 30 minutes. The samples were loaded in a capillary glass tube with a 0.3 mm outer diameter and a 0.01 mm wall thickness, and rotated during the measurements.

Magnetometry

Direct current (dc) magnetization measurements were performed using the VSM option of a QuantumDesign Dynacool Physical Property Measurement System (PPMS) equipped with a 9 T superconducting magnet in between 1.7 K and 273 K. The polycrystalline samples were loaded into standard QuantumDesign powder capsules inside an Ar-filled glovebox, sealed with wax, and mounted in a standard brass sample holder. The sample holder was transferred air-tight to the PPMS chamber and the sample space was immediately evacuated and purged with He. The experimental magnetization data were corrected for diamagnetic contributions from the sample holder and the intrinsic sample diamagnetism. Alternating current (ac) magnetization data were

acquired using the ACMS-II option (10–10,000 Hz, $H_{ac} \leq 16$ Oe) and on polycrystalline samples immobilized in polycarbonate capsules mounted in plastic drinking straws and handled as above. The paramagnetic relaxation times were extracted from the maxima of the $\chi''(\nu_{ac})$ data as $\tau^{-1} = 2\pi \nu_{ac}$.

Modelling of the magnetic properties of **Gd** was performed within the framework of the phenomenological spin-Hamiltonian formalism. Given that **Gd** can be considered as an eight-member ring made by alternating Gd(III) and bipy^{•-} and since both these species are relatively magnetically isotropic the simplest general form of spin-Hamiltonian ($\hat{H}$, Eq. 1, main text) appropriate for the phenomenological description of the magnetic properties of **Gd** should only contain terms expressing the isotropic magnetic exchange interaction between the constitutive centers and the isotropic response of the system to an external magnetic field according to the Zeeman interaction. The dimension, N , of the square matrix corresponding to the matrix representation of $\hat{H}$ for **Gd** is:

$$N = \prod_i^n (2S_i + 1) \quad \text{Eq. S1}$$

resulting in $N = 8^4 \cdot 2^4 = 65536$ for **Gd**. The magnitude of N precludes numerical diagonalization of the full spin-Hamiltonian matrix by conventional approaches¹ because of unrealistic computer memory and processor time requirements. Within the Irreducible Tensor Operator (ITO) formalism,⁷ the isotropic exchange parameter, J_{ij} , is associated to a tensor operator $\hat{O}_q^K$ of order $K = 0$ and thus, necessarily of projection $q = 0$ ($-K \leq q \leq K$, with K and q integers), since it is associated to the scalar product, $\hat{S}_i \cdot \hat{S}_j$, of the Cartesian spin-operators. The matrix elements of a tensor operator $\hat{O}_q^K$ within the coupled total spin, S , basis $|s, S, M_S\rangle$ is given by:

$$\langle s, S, M_S | \hat{O}(k, K, q) | s', S', M'_S \rangle = (-1)^{S-M_S} \begin{pmatrix} S & K & S' \\ -M_S & q & M'_S \end{pmatrix} \langle s, S || k, K || s', S' \rangle \quad \text{Eq. S2}$$

where s , s' and k are all necessary additional quantum numbers to fully define the problem, M_S is the projection of S along the quantization axis, the first term of the right-hand side is a phase, the second one is a 3- j symbol and the third is a reduced matrix element, independent of M_S . For the 3- j symbol to be non-zero a) the triangle relation has to hold for S , K and S' , from where $S = S'$, since $K = 0$; and b) $M'_S - M_S = q$, has to hold. Thus, the isotropic exchange interaction has non-zero matrix elements only between basis-function of the same total spin S . Furthermore, since for the isotropic exchange associated tensor operator $\hat{O}_q^K$, $q = 0$, the matrix element of Eq. S2 is

independent of M_S , to a phase factor of ± 1 which is irrelevant for the computation of eigenvalues. Thus, only one of the $2S+1$ projections of each total S multiplet is necessary to be included into this block-diagonal form of $\hat{H}_{iso}$, since the information contained in the $2S$ others is redundant. Finally, since $\hat{S}^2$ commutes with $\hat{S}_z$, $\hat{S}^2$ and $\hat{S}_z$ have a simultaneous eigenbasis specified by their respective eigenvalues S and M_S . This allows to transform the matrix representation of $\hat{H}$ for **Gd** into block-diagonal form, where each block corresponds to basis-functions of the same total spin S and projection M_S . Use of this methodology allows to transform the matrix representation of $\hat{H}$ for **Gd**, into block-diagonal form made up from seventeen blocks each corresponding to a total spin value S , ranging from 0 to 16, the dimensions of which are given below in Table S2.

Table S2. Total spin, S , and associated dimension, N_S , of the corresponding block in the block-diagonal form of the matrix representation of $\hat{H}$ for **Gd**.

S	N_S
16	1
15	7
14	24
13	56
12	104
11	168
10	248
9	344
8	452
7	556
6	632
5	664
4	648
3	584
2	472
1	312
0	110
sum	5382

The dimensions of the block-diagonal form of the matrix representation of $\hat{H}$ for **Gd** (Table S2) are compatible with standard numerical diagonalization approaches.⁸ The number of independent isotropic magnetic exchange parameters that can, in principle, be included in $\hat{H}$ is determined by the number of different super-exchange paths between the Gd(III) and and bipy^{•−} in **Gd**. Herein we assume a unique isotropic exchange parameter, J , since all superexchange paths are symmetry related. Additional exchange interactions originating from magnetic dipole interactions are neglected because they are usually much smaller in magnitude than the exchange interactions via

bridging ligands, as they depend inversely to the cube of the intermetallic distance. Using J as a unique fit parameter allowed the temperature dependence of the χT product and the M vs H data of **Gd** to be simultaneously numerically fitted, by use of the Levenberg-Marquardt algorithm,⁹ to the isotropic spin-Hamiltonian $\hat{H}$. This resulted in the best fit parameters $J = 0.073(4) \text{ cm}^{-1}$. Under these conditions, the spin ground state of **Gd** is an $S = 12$ (Fig. S8), separated by the first excited state, a degenerate doublet of $S = 11$ states, by only 0.16 cm^{-1} at zero magnetic field.

NIR and MIR spectroscopy

The mid-IR and near-IR direct absorption spectra were collected by a VERTEX80v Fourier transform vacuum spectrometer from Bruker Optics GmbH. Highly air-sensitive samples of polycrystalline **Gd** were sandwiched between pairs of optically transparent KBr and CaF_2 windows for the mid-IR and near-IR recordings, respectively, and subsequently sealed effectively with silicone oil at the window edges in an argon-filled glove box. The FTIR apparatus was configured with a Ge on KBr beam splitter, a liquid N_2 cooled HgCdTe detector and a thermal globar radiation source for the mid-IR single-beam measurements collected with a spectral resolution of 2 cm^{-1} . The combination of a CaF_2 beam splitter, a liquid N_2 cooled InSb detector, and a thermal tungsten lamp source was employed for the near-IR single-beam measurements collected at a spectral resolution of 3 cm^{-1} . The resulting absorbance spectra were subsequently baseline-corrected slightly and minor traces of residual water vapor absorption were subtracted.

Fig. S1. Frozen-solution (CH_3CN) X-band (9.52 GHz) EPR spectrum at 77 K of the reaction product between one equivalent of Na metal and 2.5 mol equivalent of bipy, as described in the main text.

Fig. S2. X-band (9.52 GHz) EPR spectrum at 77 K of polycrystalline **Gd** obtained at 77 K.

Fig. S3. Formation of $\{M^{III}_4(bipy^-)_4\}$ rhombi in **Gd** and **Dy** as suggested by single-crystal X-ray diffraction analysis. Color code: $bipy^-$, yellow; $bipy^0$, grey.

Table S1. Crystallographic and refinement parameters.

Compound	Gd	Gd'	Dy
CCDC number	2064815	2064816	2064814
Temperature / K	120	100	120
Crystal system	Tetragonal	Triclinic	Tetragonal
Space group	<i>I</i> 4 ₁ 22	<i>P</i> $\bar{1}$	<i>I</i> 4 ₁ 22
<i>a</i> / Å	23.2431(4)	9.1897(4)	23.1265(5)
<i>b</i> / Å	23.2431(4)	12.0159(5)	23.1265(5)
<i>c</i> / Å	33.3715(7)	14.4038(4)	33.2402(7)
α / °	90	97.506(3)	90
β / °	90	93.442(3)	90
γ / °	90	95.803(4)	90
Volume / Å ³	18028.7(7)	1564.5(1)	17778.1(9)
<i>Z</i>	16	2	16
ρ_{calc} / g cm ⁻³	1.461	1.701	1.476
μ / mm ⁻¹	20.53	29.34	20.15
Radiation	Cu K α (λ = 1.54184 Å)	Cu K α (λ = 1.54184 Å)	Cu K α (λ = 1.54184 Å)
θ range for data collection / °	4.4–75.3	3.7–76.7	3.8–76.8
Index ranges	$-29 \leq h \leq 27$	$-10 \leq h \leq 11$	$-16 \leq h \leq 28$
	$-25 \leq k \leq 19$	$-15 \leq k \leq 14$	$-29 \leq k \leq 24$
	$-41 \leq l \leq 41$	$-17 \leq l \leq 18$	$-38 \leq l \leq 41$
Reflections collected	34231	16338	28993
Independent reflections	9226 [$R_{\text{int}} = 0.073$]	6452 [$R_{\text{int}} = 0.139$]	9220 [$R_{\text{int}} = 0.061$]
Data/restraints/parameters	9226/351/528	6452/0/298	9220/372/555
Goodness-of-fit on F^2	1.04	1.06	1.04
Final R_1 index [$F^2 \geq 2\sigma(F^2)$]	0.053	0.104	0.053
Final wR_2 index [F^2]	0.150	0.282	0.139
Largest diff. peak/hole / e Å ⁻³	1.04/−1.58	3.63/−4.10	1.48/−2.10

Fig. S4. Crystal structure of **Gd** shown along the crystallographic *c* axis showing the presence of interpenetrating 2D layers.

Fig. S5. Powder X-ray diffractograms of **Gd** and **Dy** and corresponding simulations from the 120-K single-crystal X-ray structures. The grey trace is a simulation of the powder diffractogram of **Gd'** (100 K).

Fig. S6. Mid-IR/near-IR absorbance spectrum of polycrystalline **Gd** obtained at RT. The weak traces of gas-phase absorption lines around 5300–5400 cm^{-1} (combination of OH stretching fundamental + OH bending fundamental) and 7100–7200 cm^{-1} (first overtone of the OH stretching fundamental) comes from uncompensated water vapor absorption.

Fig. S7. Temperature dependence of the magnetization at selected magnetic field strengths for polycrystalline **Gd**. The turquoise solid lines are the best fit as described in the main text.

Fig. S8. Energy level spectrum of **Gd** determined as described in the main text.

Fig. S9. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility for polycrystalline **Dy** obtained with selected ac driving frequencies and in static (dc) fields of 0 T, 0.5 T, and 3 T.

Fig. S10. Frequency dependence of the in-phase (χ' , left) and out-of-phase (χ'' , right) components of the ac susceptibility for polycrystalline **Dy** obtained in selected static (dc) fields at $T = 6.5$ K.

Fig. S11. Frequency dependence of the in-phase (χ' , left) and out-of-phase (χ'' , right) components of the ac susceptibility for polycrystalline **Dy** obtained at selected temperatures and in a static (dc) fields of 3 T.

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