Incorporation of expanded organic cations in dysprosium(III) borohydrides for achieving luminescent molecular nanomagnets

Wojciech Wegner1,2*, Jakub J. Zakrzewski3, Mikolaj Zychowicz3 & Szymon Chorazy3*

Luminescent single-molecule magnets (SMMs) constitute a class of molecular materials offering optical insight into magnetic anisotropy, magnetic switching of emission, and magnetic luminescent thermometry. They are accessible using lanthanide(III) complexes with advanced organic ligands or metalloligands. We present a simple route to luminescent SMMs realized by the insertion of well-known organic cations, tetrabutylammonium and tetraphenylphosphonium, into dysprosium(III) borohydrides, the representatives of metal borohydrides investigated due to their hydrogen storage properties. We report two novel compounds, \([n\text{-Bu}_4\text{N}][\text{Dy}^{III}(\text{BH}_4)_4]\) (1) and \([\text{Ph}_4\text{P}][\text{Dy}^{III}(\text{BH}_4)_4]\) (2), involving Dy\(^{III}\) centers surrounded by four pseudo-tetrahedrally arranged \(\text{BH}_4^-\) ions. While 2 has higher symmetry and adopts a tetragonal unit cell (\(I\text{4}1/a\)), 1 crystallizes in a less symmetric monoclinic unit cell (\(P2_1/c\)). They exhibit yellow room-temperature photoluminescence related to the f–f electronic transitions. Moreover, they reveal Dy\(^{III}\)-centered magnetic anisotropy generated by the distorted arrangement of four borohydride anions. It leads to field-induced slow magnetic relaxation, well-observed for the magnetically diluted samples, \([n\text{-Bu}_4\text{N}][\text{Y}^{III}_{0.9}\text{Dy}^{III}_{0.1}(\text{BH}_4)_4]\) (1@Y) and \([\text{Ph}_4\text{P}][\text{Y}^{III}_{0.9}\text{Dy}^{III}_{0.1}(\text{BH}_4)_4]\) (2@Y). 1@Y exhibits an Orbach-type relaxation with an energy barrier of 26.4(5) K while only the onset of SMM features was found in 2@Y. The more pronounced single-ion anisotropy of Dy\(^{III}\) complexes of 1 was confirmed by the results of the ab initio calculations performed for both 1–2 and the highly symmetrical inorganic Dy\(^{III}\) borohydrides, \(\alpha/\beta\)-Dy(BH\(_4\))\(_3\) 3 and 4. The magneto-luminescent character was achieved by the implementation of large organic cations that lower the symmetry of Dy\(^{III}\) centers inducing single-ion anisotropy and separate them in the crystal lattice enabling the emission property. These findings are supported by the comparison with 3 and 4, crystalizing in cubic unit cells, which are not emissive and do not exhibit SMM behavior.

**Abstract**

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Single-molecule magnets (SMMs) form an extraordinary class of d- or f-block metal complexes exhibiting strong magnetic anisotropy which results in the slow relaxation of magnetization\(^1\text{-}^4\). Below so-called blocking temperature (\(T_B\)), they reveal a magnetic hysteresis loop of a strictly molecular origin which opens their application horizon for high-density memory devices\(^5\text{-}^6\). SMMs are also considered promising candidates for exploration in quantum computing as well as molecular spintronics\(^7\text{-}^8\). The current state of art indicates that the strongest magnetic anisotropy, thus, the best performance SMMs, is achievable by playing with lanthanide(III) complexes\(^10\text{-}^{13}\). The 4f metal centers reveal pronounced single-ion anisotropy due to the combined contributions from strong spin–orbit coupling and the crystal field effect which is much weaker but critical from the viewpoint of SMM features\(^14\). The axial distribution of negatively charged ligands around such lanthanide ions as Dy\(^{III}\), Tb\(^{III}\), or Ho\(^{III}\), is the most effective route for the generation of high-performance SMMs showing the record \(T_B\) values up to 80 K\(^16\).

**References**

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Lanthanide single-molecule magnets are attractive as they offer also distinct photoluminescent properties related to their f-f electronic transitions. Emissive lanthanide-based molecular materials arouse a broad scientific interest due to their numerous applications in such fields as optical storage, optical communication, bioimaging, chemical sensing, or optical thermometry. The construction of photoluminescence and molecular nanomagnetism is an efficient tool for better understanding of magnetic anisotropy by investigating the high-resolution emission spectra which represent the electronic structure of the ground manifold of lanthanide ions. Moreover, the bifunctionality offered by luminescent SMMs has been recently recognized to be promising from the viewpoints of the switching of emission by a magnetic field, as well as luminescent thermometry for electromagnetic SMM-based devices exhibiting the self-monitoring of temperature.

There are several synthetic pathways which were employed for achieving luminescent single-molecule magnets, mainly based on visible light-emissive DyIII and TbIII centers, NIR-emissive YbIII or NdIII centers, or realized by the application of organic ligands as an emission source. The majority of synthetic strategies applied in the construction of emissive SMMs take advantage of expanded organic ligands which are responsible both for constraining the coordination geometry of 4f metal ions towards strong single-ion anisotropy as well as sensitizing its luminescence through ligand-to-metal energy transfer. Alternatively, luminescent molecular nanomagnets can be obtained by the incorporation of lanthanide ions into coordination frameworks, including metal–organic frameworks, based on organic linkers or d-block metallo ligands. The up-to-date reported routes toward emissive SMMs explore rather sophisticated lanthanide(III) moieties exploring complicated organic ligands or a multi-component approach demanding the second metal complex.

Therefore, there is an attractive perspective in searching for simpler organic or inorganic molecular systems involving lanthanide(III) centers that can serve as luminescent molecular nanomagnets. In this context, we decided to test lanthanide(III) borohydrides as a possible source of luminescent SMMs.

The history of metal borohydrides starts in 1939 with the synthesis of the first member of this family, Al(BH4)3. Interest in such systems was accelerated by the Manhattan Project, during which e.g. volatile actinide borohydrides were studied. These studies laid the foundations for borohydride chemistry, by i.a. synthesis of NaBH4 and KBH4 or preparation of other metal borohydrides using metathetic reactions on alkali metal borohydrides. Since then, metal borohydrides were broadly investigated, mainly as reductive agents in chemical synthesis. In the last 2 decades, the chemistry of metal borohydrides flourished again, as new metal borohydride systems were found promising as chemical hydrogen storage materials for fuel-cell vehicles. Synthesis of new systems was also stimulated due to their various other properties, as metal borohydrides can serve as e.g. solid-state electrolytes in Li+ batteries, organic catalysts, precursors of metal borides, or even boron nitride. Lately, borohydrides of rare earth metal (RE) ions have been reported among them, binary yttrium borohydride is well-known and crystallizes in the same α-/β-RE(BH4)3 forms as lanthanide borohydrides. In general, homoleptic lanthanide borohydrides crystallize in three polymorphic forms: r-RE(BH4)3 for RE = La, Ce, Pr, Tb, Ho, with trigonal unit cell; a-RE(BH4)3 and β-RE(BH4)3 for RE = Ce67,72, Pr, Nd, Sm, Eu, Gd68, Tb71, Dy69, Ho70, Er71, Tm72, Yb72, Lu72, with cubic unit cells. The homoleptic RE(BH4)3 (with (RE)) compounds are also known for RE = Eu, Sm, Yb, Y. The interest was also devoted to mixed cation borohydrides, containing lanthanide ions accompanied with alkali metal ions or organic groups. Rare earth borohydrides can exhibit strong photoluminescent properties originating from f-f or d-f electronic transitions, as was exemplified by α-Tb(BH4)3 and the perovskite-type RE2+ borohydrides, KYb(BH4)3 and CsEu(BH4)3, together with CsCa(BH4)3:Eu2+. The history of lanthanide borohydrides was recognized in this family, the generation of magnetic anisotropy by using lanthanide borohydrides is a more challenging task as they usually crystallize in space groups of high symmetry with a rather isotropic coordination environment around 4f metal center. Moreover, a non-negligible super-exchange coupling was lately reported for both α-RE(BH4)3 and β-RE(BH4)3, RE = Gd, Tb, Dy, Ho, Er, Tm, along with KHo(BH4)3, RbTm(BH4)3, and MYb(BH4)3, M = Li, Na, showing that [BH4]− is capable of mediating both weakly ferro- and antiferromagnetic super-exchange. All these features are well-known to cancel the SMM effect of a single ion origin. To overcome these difficulties, we decided to employ expanded organic cations, tetraethylammonium (n-Bu4N+) and tetraphenylphosphonium (Ph4P+) for the construction of organic lanthanide(III) borohydrides to decrease the overall crystal symmetry and distort the geometry of 4f metal complexes. These are expected to generate distinct single-ion anisotropy and better magnetic isolation within the crystal lattice. We decided to explore Dy(III) complexes which are yellow-to-white emissive as a result of the characteristic f-f electronic transitions, and found to be highly anisotropic in diverse coordination environments.

As a result, we report the synthesis, crystal structures, magnetic and photoluminescent properties of two novel organic dysprosium(III) borohydrides, [n-Bu4N][DYIII(BH4)4] (1) and [Ph4P][DYIII(BH4)4] (2), first known derivatives of Dy(BH4)3, together with their magnetically YIII-diluted analogs, [n-Bu4N][YIII0.9DyIII0.1(BH4)4] (1@Y) and [Ph4P][YIII0.9DyIII0.1(BH4)4] (2@Y). They serve as luminescent molecular nanomagnets combining room-temperature DyIII-centered luminescence with a field-induced slow magnetic relaxation effect related to the intrinsic single-ion anisotropy of DyIII centers surrounded by four borohydride anions. For the comparison, we also prepared and tested simple inorganic dysprosium(III) borohydrides, α/β-Dy(BH4)3, which do not reveal any luminescent or SMM features.

**Methods**

**Synthesis, sample handling protocol, and chemicals used.** All reactions, together with the sample storage and handling, were performed under an argon atmosphere in gloveboxes, with O2 and H2O levels < 1 ppm. All used reagents were anhydrous, of a high purity, purchased from Sigma-Aldrich: DyCl3, YCl3 > 99.99%; LiBH4 > 95%; (C2H5)3P (Ph3P) > 98%; (C2H5)2CHCH2CH2)2N(BH4) (n-Bu4NBH4) > 98%. Anhydrous dichloromethane (DCM), purchased from Sigma-Aldrich, was distilled over P2O5 and placed inside glovebox with the addition of molecular sieves. Mechanocohemical reactions, using high energy milling method, were carried out in
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Table 1. Chemical composition of described compounds, their synthesis protocols, and used substrates.

| Sample symbol | Substrates (mmol) | Synthesis protocol | Crystalline products |
|---------------|------------------|--------------------|---------------------|
| 1             | 1 [n-Bu4N]BH4, 1 DyCl3, 3 LiBH4 | 12×5 min milling (5) | [n-Bu4N][Dy(BH4)4], LiCl |
| 1@Y           | 1 [n-Bu4N]BH4, 0.1 DyCl3, 0.9 YCl3, 3 LiBH4 | 12×5 min milling (6), recrystallization and decantation from DCM | [n-Bu4N][Y0.9Dy0.1(BH4)4], LiCl |
| 2             | 1 [Ph4P]Cl, 1 DyCl3, 4 LiBH4 | 12×5 min milling (3) | [Ph4P][Dy(BH4)4], LiCl |
| 2@Y           | 1 [Ph4P]Cl, 0.1 DyCl3, 0.9 YCl3, 4 LiBH4 | 12×5 min milling (4), recrystallization from DCM | [Ph4P][Y0.9Dy0.1(BH4)4] |
| 3             | 1 DyCl3, 3 LiBH4 | 4×5 min milling (1) | α-Dy(BH4)3, LiCl |
| 4             | 1 DyCl3, 12 LiBH4 | 12×5 min milling (2) | 0.9 β-/0.1α-Dy(BH4)3, LiCl, LiBH4 |

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| 1@Y           | 1 [n-Bu4N]BH4, 0.1 DyCl3, 0.9 YCl3, 3 LiBH4 | 12×5 min milling (6), recrystallization and decantation from DCM | [n-Bu4N][Y0.9Dy0.1(BH4)4], LiCl |
| 2             | 1 [Ph4P]Cl, 1 DyCl3, 4 LiBH4 | 12×5 min milling (3) | [Ph4P][Dy(BH4)4], LiCl |
| 2@Y           | 1 [Ph4P]Cl, 0.1 DyCl3, 0.9 YCl3, 4 LiBH4 | 12×5 min milling (4), recrystallization from DCM | [Ph4P][Y0.9Dy0.1(BH4)4] |
| 3             | 1 DyCl3, 3 LiBH4 | 4×5 min milling (1) | α-Dy(BH4)3, LiCl |
| 4             | 1 DyCl3, 12 LiBH4 | 12×5 min milling (2) | 0.9 β-/0.1α-Dy(BH4)3, LiCl, LiBH4 |

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| 2             | 1 [Ph4P]Cl, 1 DyCl3, 4 LiBH4 | 12×5 min milling (3) | [Ph4P][Dy(BH4)4], LiCl |
| 2@Y           | 1 [Ph4P]Cl, 0.1 DyCl3, 0.9 YCl3, 4 LiBH4 | 12×5 min milling (4), recrystallization from DCM | [Ph4P][Y0.9Dy0.1(BH4)4] |
| 3             | 1 DyCl3, 3 LiBH4 | 4×5 min milling (1) | α-Dy(BH4)3, LiCl |
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| 1@Y           | 1 [n-Bu4N]BH4, 0.1 DyCl3, 0.9 YCl3, 3 LiBH4 | 12×5 min milling (6), recrystallization and decan...
Physical properties measurements and computational details. Alternate-current (ac) and direct-current (dc) magnetic measurements were performed using a Quantum Design MPMS 3 SQUID magnetometer with an Evercool system. Samples during the measurements were placed in the hermetic FEP capsules under an Ar atmosphere. Excitation and emission spectra were recorded on the Edinburgh Instruments F55 spectrofluorometer equipped with a Xe arc lamp as an excitation source and a Hamamatsu photomultiplier as a detector. Computational details regarding the ab initio calculations of CASSCF/RASSI/SINGLE_ANISO type (together with the related references) performed on the experimental crystal structures of 1–4 were discussed in the Supporting Information.

Results and discussion

Synthesis outcome and crystal structures. \([n\text{-Bu}_4\text{N}][Y_{1-x}Dy_x(BH_4)_4] \quad (1, \ x = 1; \ 1@Y, \ x = 0.1) \) and \([\text{Ph}_4\text{P}][Y_{1-x}Dy_x(BH_4)_4] \quad (2, \ x = 1; \ 2@Y, \ x = 0.1)\). Unit cells of \([\text{Cat}][\text{Dy}(BH_4)_4]\), \([\text{Cat}] = n\text{-Bu}_4\text{N}^+\) (sample 1) and \(\text{Ph}_4\text{P}^+\) (sample 2) are presented in Fig. 1, along with \([\text{Dy}(BH_4)_4]^-\) geometries. They are constructed of alternating \([\text{Cat}]^+\) and \([\text{Dy}(BH_4)_4]^-\) ionic building blocks. The \([\text{RE}(BH_4)_4]^-\) moiety is observed in almost all known derivatives of rare-earth (RE) borohydrides. Each BH_4^- group is serving as a tridentate ligand to REIII (DyIII) metal center, leading to quasi 12-coordinated complexes. The crystal structure of 2 has higher symmetry and adopts a tetragonal unit cell (space group \(I4_1/a\)), while 1 crystallizes in the monoclinic unit cell (\(P2_1/c\)). In both structures, there is only one symmetrically independent cation (\(\text{Ph}_4\text{P}^+\) or \(n\text{-Bu}_4\text{N}^+\)) and one independent anion \([\text{Dy}(BH_4)_4]^-\). Additionally, in 2, there is only one independent BH_4^- group according to symmetry restraints, while in 1, there are four of them, which leads to the deformed geometry of \([\text{Dy}(BH_4)_4]^-\) in 1 (Fig. 1). In the supramolecular framework of 1, the \([\text{Dy}(BH_4)_4]^-\) unit is surrounded by nitrogen centers of four \([n\text{-But}_4\text{N}]^+\) cations forming a...
form, α-[n-Bu4N][REIII(BH4)4]81,82,88. The latter is observed in the case of α-Dy(BH4)3. Both LiCl (a by-product of the synthesis) and LiBH4 (used in excess in the reaction), present in the α-Dy(BH4)3 and β-Dy(BH4)3 polymorphs, which results in the lowering of local susceptibility–temperature products, \(\chi \cdot T\), are shown in Figure S1. Room-temperature values of magnetic susceptibility are presented in Table 1. In \(\beta\)-Dy(BH4)3 and \(\beta\)-Dy(BH4)4, the only Dy-based phase is α-Dy(BH4)3, while bigger ones (Tm, Ho, Y) tend to crystallize in lower symmetric compounds. The latter is observed in the case of 1 and 1@Y, further confirming the reported trend.

α-Dy(BH4)3 and β-Dy(BH4)3. Crystal structures and synthesis protocols for simple dysprosium borohydrides, α-Dy(BH4)3 (3) and β-Dy(BH4)3 (4), were described before. Chemical compositions of these samples are presented in Table 1. In 3, the only Dy-based phase is α-Dy(BH4)3, while 4 includes 90% of β- and 10% of α-Dy(BH4)3. Both LiCl (a by-product of the synthesis) and LiBH4 (used in excess in the reaction), present in these samples, are magnetically and luminescent inactive. Both α-Dy(BH4)3 and β-Dy(BH4)3 crystal structures consist of alternately arranged DyIII and BH4– units (Figure S17). They both adopt cubic unit cells, where six borohydride groups form octahedrons around each DyH3. This octahedron is regular in the case of α-Dy(BH4)3 and slightly distorted in the case of α-Dy(BH4)4 polymorph, which results in the lowering of local symmetry and slightly smaller Dy–Dy distances. Each borohydride group is shared between two dysprosium ions, coordinating each Dy3+ with two hydrogen atoms, leading to quasi 12-coordinated Dy centers. For the comparison, we analyzed inorganic and organic derivatives of scandium borohydride, [Cat][Sc(BH4)4], [Cat] = Li89, Na90, K91, NH292, Rub, Ca93, Me4N, n-Bu4N and Ph4P93, derivatives of yttrium borohydride, [Cat][Y(BH4)4], [Cat] = Li, Na94, K95, NH292, Rub, Ca96, Me4N97, n-Bu4N98, and known derivatives of lanthanide borohydrides, [Cat][RE(BH4)4], with RE = Er, [Cat] = Na99, K100, RE = Ho, [Cat] = K101; RE = Tm, [Cat] = Ph4P102; Rub or RE = Yb, [Cat] = Li98, Na101, K4. Based on this analysis, [Cat] = n-Bu4N derivatives (including 1) have the longest RE–BH distances and the lowest unit cell symmetry. In the majority of cases, simple borohydrides have the shortest distances between RE centers. This trend is well illustrated in the obtained compounds (Table 2).

### Table 2. Crystal data of 1 and 2, and their Y-diluted analogs, compared with the reported 3 and 4.

| Compound | 1 | 1@Y | 2 | 2@Y | 3 | 4 |
|----------|---|-----|---|-----|---|---|
| Composition | [n-Bu4N][Dy(BH4)4] | [n-Bu4N][Y0.9Dy0.1(BH4)4] | [Ph4P][Dy(BH4)4] | [Ph4P][Y0.9Dy0.1(BH4)4] | α-Dy(BH4)3 | β-Dy(BH4)3 |
| Space group | P 2/c | P 2/c | P 2/c | P 2/c | P 3 | P m 3 |
| \(a\) [Å] | 11.4240(10) | 11.4464(7) | 14.373(2) | 14.3854(5) | 10.8866(5) | 11.05958(14) |
| \(b\) [Å] | 12.9478(8) | 12.9468(4) | 14.373(2) | 14.3854(5) | 10.8866(5) | 11.05958(14) |
| \(c\) [Å] | 90 | 90 | 90 | 90 | 90 | 90 |
|\(\beta\) [°] | 90 | 90 | 90 | 90 | 90 | 90 |
|\(\gamma\) [°] | 90 | 90 | 90 | 90 | 90 | 90 |
|\(Z\) | 4 | 4 | 4 | 4 | 8 | 8 |
| Dy–Dy [Å] | 8.127(9) | – | 7.9459(10) | – | 5.4880(4) | 5.52979(8) |

Magnetic properties: experiment and ab initio calculations. Direct-current (dc) magnetic properties for the powder samples of 1 and 2 are shown in Figure S1. Room-temperature values of magnetic susceptibility–temperature products, \(\chi \cdot T\), are 14.5 and 14.3 cm3 mol–1 K for 1 and 2, respectively, which are very close to the value of 14.2 cm3 mol–1 K, expected for the free-ion contribution from the single Dy3+ ion with its \({^6}H_{15/2}\) ground multiplet. Upon cooling, the \(\chi \cdot T\) values gradually decrease, slowly in the 300–50 K range and more abruptly below this point. This behavior can be assigned to the DyIII single-ion property, that is the thermal depopulation of the \(m_l\) levels within the ground manifold. However, non-negligible magnetic interactions between Dy metal centers, operating at low temperatures, cannot be excluded. They are rather weak due to the long Dy–Dy distances of 8.1 and 7.9 Å in 1 and 2, respectively, but they cannot be fully neglected as the \(\chi \cdot T\) value drops quite abruptly in the lowest temperature regime reaching 6.9 cm3 mol–1 K at 1.8 K, which is a relatively small value when compared with typical magnetically isolated DyIII complexes. Magnetic interac-



tions for 3 and 4 were described before. They are of a weak ferromagnetic character with exchange constant, $J$, of 0.018 and 0.033 cm$^{-1}$, respectively (ferromagnetic character of the latter was confirmed by DFT calculations). 3 and 4 are built of Dy$^{III}$ centers with intermetallic distances of ca. 5.5 Å enforced by bridging BH$_4^-$ ions, while in 1 and 2 [Dy(BH$_4$)$_4$]$^{II}$ moieties are isolated by organic cations. The latter causes the increase of Dy–Dy distances by almost 50%, compared to inorganic salts, which reduces magnetic interactions. Magnetic-field-dependence of magnetization for 1 and 2 collected at $T$ = 1.8 K reveals the featureless increase of the signal without full saturation even for the strong field of 7 T. This indicates the presence of non-zero magnetic anisotropy of Dy$^{III}$ centers embedded in 1 and 2. The highest achievable magnetization values of 5.9 and 6.1 μ$_B$ for 1 and 2, respectively, are within the typical range of 5–6 μ$_B$ observable for magnetically anisotropic Dy$^{III}$ complexes. Magnetic hysteresis loops are not observed (Figure S2). The presence of significant magnetic anisotropy and/or low-lying excited states in 1 and 2 is also supported by the non-superposition of the reduced magnetization curves gathered at low temperatures below 5 K (Figure S3).

To examine the expected slow magnetic relaxation effect related to the presence of Dy$^{III}$ moieties, alternate-current (ac) magnetic properties of 1 and 2 were investigated. Under zero dc field, even at the very low temperature of 1.8 K, 1 does not reveal any noticeable signal of the imaginary part of magnetic susceptibility, $\chi''$. The $\chi''$ signal appears in the form of the high-frequency tail after applying a small dc field of 200 Oe (Figure S4). On the increasing dc field in the 200–1000 Oe range, the $\chi''$-tail in the 10–1000 Hz improves but a further increase of the dc field leads to the disappearance of this relaxation. Such behavior may suggest the field-induced onset of some slow magnetic relaxation process related to the single-ion property of Dy$^{III}$ appearing thanks to the canceling of the QTM effect at low fields and the further appearance of a direct process. To verify this hypothesis, we examined the $T$-dependence of the ac signal for the optimal dc field of 1 kOe. We found the gradual decreasing of the high-frequency $\chi''$-tail from 1.8 to 3.0 K. No clear maxima were detected, thus, only the simplified approach based on the linear fragments of the ln($\tau$) versus $T^{-1}$ plots was used. Pardo et al., was used. It gives the roughly estimated effective energy barriers related to the Arrhenius-type relaxation pathways. In 1 at 1 K, we found two linear parts of the ln($\chi''/\chi''_0$) versus $T^{-1}$ plots, operating at lower and higher temperatures, which indicate the presence of two effective energy barriers. However, they are very small, ca. 1.7 and 2.3 K, which is much below the limits for the typical Orbach relaxation of SMM systems. This suggests that the observed onset of magnetic relaxation is not of a pure single-ion origin, presumably affected by the non-negligible magnetic interactions between Dy centers. Such interpretation is supported by the appearance of the second, slower relaxation pathway at higher dc fields above 1.5 kOe as visualized by the new $\chi''$ maxima in the 1–10 Hz range. We found that the related relaxation time, found from the ac signal following the generalized Debye model (Figure S5), is only weakly temperature-dependent as the increased temperature mainly leads to the weakening of the signal. The resulting $T$-dependence of relaxation time was also described by two linear fragments assignable to the Arrhenius-type processes but the very low energy barriers, ca. 2.5 and 7.2 K, accompanied by the unusually large $\tau$ values above $10^{-5}$ s, were determined (Table S1). This indicates that both relaxation processes detected in 1 should be ascribed mainly to dipolar interactions between insufficiently separated Dy centers.

Therefore, we decided to prepare and investigate the magnetically diluted sample, 1@Y, where Dy$^{III}$ complexes are embedded in the diamagnetic Y$^{III}$-based matrix (Fig. 2 and S6–S7). Even at the lowest temperature of 1.8 K, 1@Y does not exhibit slow magnetic relaxation at zero dc field, however, the clear $\chi''$ maxima appear after applying even the small dc field of 200 Oe (Fig. 2i). Starting from this field up to 2 kOe, the $\chi''$ signal following the generalized Debye model (Figure S5), is only weakly temperature-dependent as the increased temperature mainly leads to the weakening of the signal. The resulting $T$-dependence of relaxation time was also described by two linear fragments assignable to the Arrhenius-type processes but the very low energy barriers, ca. 2.5 and 7.2 K, accompanied by the unusually large $\tau$ values above $10^{-5}$ s, were determined (Table S1). This indicates that both relaxation processes detected in 1 should be ascribed mainly to dipolar interactions between insufficiently separated Dy centers.

The first term represents the Orbach relaxation characterized by a thermal energy barrier, $\Delta E/k_B$, and the relaxation attempt time, $\tau_0$. The second term is related to the direct process for a Kramers ion, depicted by the single parameter, $A$. The next term represents the Raman relaxation with two variable parameters, $B_{\text{Raman}}$ and the power $n$, adopting the values smaller or equal to 9 for the Kramers ions. The last term is related to the QTM effect which is only field-dependent and described by two parameters, $B_1$ and $B_2$. To make an attempt on a reliable fitting following the Eq. (7), we applied the simultaneous fit of both field (Fig. 2i) and temperature dependences (Fig. 2v) of relaxation times. Even with this restriction, the number of accessible parameters is high (seven), thus, we considered various combinations of relaxation processes (Figs. 2v and S8, Tables S1–S2). The $\tau$ versus $H$ dependence reveals the characteristic shape with the maximum around the optimal dc field of 1 kOe which can be interpreted in terms of the initial quenching of QTM and the further generation of a direct process. Therefore, we took into account two related contributions to the overall magnetic relaxation depicted by the parameters $A$, $B_1$, and $B_2$, in which starting values were taken from the separate preliminary fit of the $\tau$ versus $H$ plot. With this assumption, we tested the combination of QTM and direct processes together with Orbach or Raman
relaxation processes. We found the successful fitting results by using three relaxation processes, QTM, direct, and Orbach (Figs. 2i, 2v). The best-fit parameters are $\Delta E/k_B = 24.6(5)$ K, $\tau_0 = 7(2) \times 10^{-10}$ s, $A = 1.58(3) \times 10^{-10}$ s$^{-1}$ K$^{-1}$ Oe$^{-4}$, $B_1 = 2619(136)$ s$^{-1}$, and $B_2 = 4.1(6) \times 10^{-6}$ Oe$^{-2}$. The parameters for Orbach relaxation, $\Delta E/k_B$ and $\tau_0$, are within the ranges characteristic of lanthanide SMMs, however, of a rather weak magnetic anisotropy. The alternative fitting employing Raman relaxation, instead of Orbach process, along with QTM and direct relaxation routes, was excluded as it resulted in the unrealistically high power $n$ of 12.9(3) for the Raman process, while the fixed power $n$ of 9 leads to the poor quality of the fitting (Figure S8 and Table S2). As the observed contributions

**Figure 2.** Dynamic (ac) magnetic properties of 1@Y (left) and 2@Y (right): dc-field-variable frequency dependences of the out-of-phase susceptibility, $\chi_M''$ of 1@Y (i) and 2@Y (ii) gathered in the 200–2500 Oe range at 1.8 K, and the related field dependence of the relaxation time for 1@Y (i), temperature-variable frequency dependences of the $\chi_M''$ of 1@Y (iii) and 2@Y (iv) collected in the 1.8–2.1 K range at $H_{dc} = 1$ kOe, the related temperature dependence of the relaxation time for 1@Y (v), and the ln($\chi_M''/\chi_M'$) versus $T^{-1}$ plots for the indicated frequencies of ac field (v). The empty colored points in the frequency dependences of the $\chi_M''$ (i–iv) represent the experimental data. The solid lines in the respective curves of 1@Y (i and iii) show the fitting according to the generalized Debye model while the analogous lines for 2@Y (ii and iv) are only to guide the eye. The solid lines in the field- (i, green line) and temperature-dependences (v, dark red) of the relaxation time of 1@Y represent the best-fit curve of the combined contributions from QTM, direct, and Orbach relaxation routes, while the black points show the experimental data. The light green line in (v), together with the green-colored text, represents the best-fit curves according to the Arrhenius law (the first term in the Eq. 7). The contributions from each type of relaxation were depicted in (v) as dotted lines. In the ln($\chi_M''/\chi_M'$) versus $T^{-1}$ plots of 2@Y (vi), the black points show the experimental data while the solid red lines are the best-fit curves for a simplified approach elucidating the Arrhenius-type relaxation with the depicted effective energy barrier.
from QTM and direct processes to the overall magnetic relaxation (Fig. 2v) are weak, we also examined the fitting procedures without these two processes. In this context, we found that Raman relaxation cannot reliably describe the $T$-dependence of relaxation time due to the unrealistic parameters or poor fitting quality (Figure S8 and Table S2) while the sole Orbach relaxation relatively well represent the experimental data giving the slightly decreased energy barrier of 19.7(4) K accompanied by the pre-exponential factor of 7.2(13) $10^{-5}$ s (Figs. 2v and S8e). These last values correspond to the simple Arrhenius law (the first term in the Eq. 7), thus they give insight into the effective energy barrier ($U_{ac}$) and the pre-exponential factor ($\tau_0$) which were found to be typical for moderate Dy(III) SMMs. Nevertheless, the above-presented analyses suggest that the borohydride DyIII complexes of 1@Y at the accessible temperature regime (1.8–2 K) exhibits three relaxation processes, QTM, direct, and the dominant Orbach. The determination of other possible relaxation, a Raman process, is not achievable due to the limited temperature range. Only the access to lower than the 1.8 K temperatures for ac measurements may elucidate this issue.

Qualitatively similar ac dynamic properties were detected for 2 and its magnetically diluted sample, 2@Y (Figs. 2 and S9–S10). Similarly to 1, compound 2 exhibits the field-induced ac magnetic signal. However, it appears only in the low-frequency region below 50 Hz as the signal tails without the clear maximum in the range of 0.5–1000 Hz (Figure S9). We followed the $T$-dependence of this magnetic relaxation for the optimal $dc$ field (i.e. those of the strongest $\chi''_{ac}$ signal) of 1 Koe finding the gradual disappearance of the $\chi''_{ac}$ tails without any frequency shifts. Therefore, the observed relaxation process in 2 was assigned to the dipolar interactions between DyIV centers. The lack of any ac signal in the higher frequency range, as was detected in 1, suggests that the magnetic interactions between 4f metal ions are even stronger than in 1 which stays in good agreement with structural data indicating shorter Dy–Dy distances in 2. Thus, to examine the intrinsic single-ion anisotropy of DyIV in 2, we investigated the ac magnetic properties for the YIV-diluted sample of 2@Y (Figs. 2 and S10). Thanks to the magnetic dilution effect, 2@Y exhibits the field-induced magnetic relaxation under very similar field and temperature conditions as observed in 1@Y. However, the relaxation processes are slightly accelerated which results in the observation of only the onset of slow magnetic relaxation in the high-frequency region (Fig. 2ii, iv). Therefore, it was not possible to apply the generalized Debye model to fit the ac magnetic curves and determine the related magnetic relaxation times. We only applied the simplified approach based on the linear parts of the In($\chi''_{ac}/\chi''_{dc}$) versus $T^{-1}$ plots (Fig. 2vii)103,104. These dependencies were linear in the whole accessible temperature range related to the onset of the $\chi''_{ac}$ signal enabling the determination of the effective energy barrier of the Arrhenius-type thermal relaxation pathway. The resulting $U_{ac}$ of 20.1(3) K is comparable with the energy barrier of 26.4(5) K for Orbach relaxation in 1@Y suggesting the analogous single-ion origin of slow magnetic relaxation. Its smaller value indicates that the intrinsic magnetic anisotropy of DyIV in 2 is weaker than in 1. This can be correlated with more axial character of the 4f metal complexes in 1 which can be related to its lower crystal symmetry (Table 2). Even that the magnetic dilution in 1@Y and 2@Y improves the slow magnetic relaxation effects, the magnetic hysteresis at the lowest accessible temperature of 1.8 K is not observed for any of the magnetically diluted samples (Figure S2) which is related to very weak single-ion anisotropy of investigated DyIV centers. We also checked 3 and 4 for the SMM behavior but ac measurements point out they do not exhibit SMM features that can be assigned to short distances between DyIV centers and higher unit cell symmetry.

For the additional proof for the appearance of magnetic anisotropy in organic DyIV borohydrides of 1 and 2, we performed the ab initio calculations of CASSCF/RASSI/SINGLE_ANISO type which are currently the most powerful computational tool for the analysis of single-ion anisotropy of lanthanide molecular nanomagnets (see the computational details in the Supporting Information)28,29,106. The ab initio calculations were performed on the experimental crystal structures of 1–4 consisting of the DyIV centers with the directly attached borohydride ions, four in the case of 1–2, and six in the case of 3–4 (Figure S11). For comparative analysis within the whole series of 1–4, two different basis sets, small S and large L, differing in the basis function qualities, were employed (Table S3). The obtained results are gathered in Tables S4–S7. From these results, it is clearly seen that 1 exhibits a distinct single-ion anisotropy of DyIV centers represented by the axial ground Kramers doublet with the high $g_z$ value of ca. 19.5 which is characteristic for the [+ 15/2] $m_l$ state dominant within the ground multiplet (Table S4). The magnetic easy axis of the ground multiplet is situated nearly along the Dy–B direction related to the borohydride revealing the closest distance to the metal ion (Figure S11) which indicates that the asymmetric arrangement of borohydride ions and their variable distances to the 4f metal ion are responsible for the induction of lanthanide magnetic anisotropy. It is, however, imperfect as there is a non-negligible admixture of other $m_l$ states to the ground doublet which gives rise to the $g_x, g_y$ values above 0.025. As a result, the strong QTM effect is generated which finds the reflection in the ac magnetic data showing that the SMM character is observed only under the applied $dc$ magnetic field (Fig. 2). The first excited Kramers doublet is lying ca. 100 cm$^{-1}$ above and reveals the much less axial character, thus it can be involved in the Orbach relaxation pathway. However, its energy position is much higher than the experimental energy barrier of 26.4(5) K (18.4(4) cm$^{-1}$) found for the contribution from an Orbach process. This can be only partially ascribed to the underestimation of the experimental energy barrier due to the unresolved admixture of Raman relaxation process (see above). Thus, this difference can be mainly explained by the uncertainty of the critical Dy–B and Dy–H distances in the crystal structure used for the ab initio calculations as it comes from the PXRD analysis, which is much less accurate that the structural models from the single-crystal X-ray analyses, usually employed for this type of calculations106. Nevertheless, the generation of a significant single-ion anisotropy of DyIV centers in 1 is supported by the obtained results of the ab initio calculations. This is particularly depicted by the comparison with the computed DyIV crystal-field effects in the highly symmetrical inorganic DyIV borohydride complexes of 3 and 4 (Tables S6–S7). In the large basis L, both 3 and 4 exhibit an easy-plane type of DyIV magnetic anisotropy on the ground Kramers doublet characterized by the highly mixed $m_l$ composition. This agrees well with the lack of ac magnetic signal in these two compounds and can be straightforwardly correlated with the high symmetry of the related DyIV complexes with six closely positioned borohydride anions (Figure S11). We also performed the ab initio calculations for...
(Fig. 1), and stays in a good agreement with the experiment showing only the onset of distances detected in slow magnetic relaxation on than observed in 1 which can be correlated with the presence of four identical Dy–B distances in 2 while four different Dy–B distances detected in 1 (Fig. 1), and stays in a good agreement with the experiment showing only the onset of slow magnetic relaxation on 2 even under the optimal dc field (Fig. 2). It suggests that the deformation of Dy III complexes towards an asymmetric arrangement of borohydrides in 1 plays a critical role, more important than the generally decreased crystal symmetry occurring going from 3–4 to 1 and 2.

Luminescence properties. Due to the very weak visible light absorption, and the intrinsic photoluminescent character of Dy III ions, we investigated solid-state UV-induced emission properties of 1 and 2 at both room and liquid nitrogen temperatures (Figs. 3 and S12). At 298 K, under the UV light irradiation, 1 and 2 exhibit yellow emission mainly related to the strong sharp peak centered at 576 nm (Fig. 3ii). This dominant emission band is accompanied by a series of much weaker peaks at ca. 490, 665, and 750 nm. All of them can be assigned to the f–f electronic transitions of Dy III occurring from the emissive 4F9/2 level to the lower-lying 6H15/2, 15/2, 11/2, 9/2 multiplets25. It results in the overall yellow emission depicted by the CIE 1931 chromaticity parameters of (0.46, 0.46), almost identical for 1 and 2 (Fig. 3). The rich excitation patterns (Fig. 3i), consisting of the series of sharp peaks rather than the broad bands, indicate that the emission properties are due to the direct f–f excitation pathways as these excitation peaks can be assigned to the specific electronic transitions from the ground 4H15/2, 15/2, 11/2, 9/2 multiplet to the higher-lying excited states within the Dy III centers107. There is no proof for an intermolecular energy transfer process which could be expected particularly for 2 incorporating expanded Ph4P+ cations. Nevertheless, yellow photoluminescence both in 1 and 2 was detected at room temperature. It remains almost unchanged on cooling to the liquid nitrogen (Figure S12), again suggesting that the additional energy transfer processes are not observed and the luminescence can be ascribed to the single-ion property of Dy III ions. As a result, the YIII-diluted samples were not expected to produce extra emission features, except of their magnetically YIII-diluted analogs, [n-Bu4N][Y0.9Dy0.1(BH4)4] and [Ph4P][Y0.9Dy0.1(BH4)4]. The most pronounced single-ion anisotropy of Dy III complexes was observed in the lowest symmetrical phase of [n-Bu4N][Dy(BH4)4] which was confirmed by the results of the ab initio calculations performed along the whole series of discussed compounds. Moreover, the obtained organic Dy(III) borohydrides serve as luminescent molecular
nanomagnets, which combine room-temperature lanthanide-based photoluminescence in the solid-state with a field-induced slow magnetic relaxation effect. Their yellow luminescence was achievable due to the absence of solvent molecules and colored chromophore components, as well as the sufficient separation of 4f metal ions within the crystal lattice. This interpretation is supported by the investigation of α/β-Dy(BH$_4$)$_3$ phases which do not reveal any luminescent features. They are also magnetically isotropic without any sign of the SMM character. It means that Dy$^{3+}$ magnetic anisotropy is generated by the low-symmetry coordination environment observed in the organic derivatives. Therefore, this work shows a simple route to luminescent SMMs realized by the insertion of well-known organic cations, tetrabutylammonium and tetraphenylphosphonium, into Dy(III) borohydrides. Such simple modification of classical inorganic borohydrides was found to be efficient in inducing attractive optical and magnetic properties. Future work can be focused on the further functionalization of lanthanide(III) borohydrides using chiral and/or polar organic cations which can enrich multifunctional potential towards chiral or ferroelectric luminescent SMMs.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

All authors wrote and reviewed the manuscript, as well as performed together magnetic and luminescence analysis. W.W. synthesized samples, performed Rietveld refinements, conducted the related experiments, and applied for funding.

Competing interests

The authors declare no competing interests.
