Supporting Information for:

Sublimable chloroquinolinate lanthanoid single-ion magnets deposited on ferromagnetic electrodes

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1. Synthesis

Figure SI1: Scheme of the ligand 5,7-dichloro-8-hydroxyquinoline (5,7Cl₂q).
### Table SI1: Crystallographic data for the compounds.

| Identification code | NaLnClq (3) | NEtDyClq (4) | KNEtDyClq (5) |
|---------------------|-------------|--------------|--------------|
| Empirical formula   | C_{39}H_{23}Cl_8DyN_5NaO_5 | C_{44}H_{36}Cl_8DyN_5O_4 | C_{84}H_{58}Cl_{16}Dy_2KN_{11}O_8 |
| Formula weight      | 1110.71     | 1144.88      | 2280.71      |
| Temperature/K       | 120(2)      | 120(2)       | 120(2)       |
| Crystal system      | Monoclinic  | Monoclinic   | Triclinic    |
| Space group         | P2\_1/c    | C2/c         | P-1          |
| a/Å                 | 9.9819(2)   | 36.1061(11)  | 15.8989(16)  |
| b/Å                 | 19.8256(4)  | 11.5705(3)   | 16.0286(16)  |
| c/Å                 | 20.6783(4)  | 22.7831(6)   | 19.542(2)    |
| α/°                 | 90          | 90           | 98.384(9)    |
| β/°                 | 91.212(2)   | 109.429(3)   | 91.201(9)    |
| γ/°                 | 90          | 90           | 118.115(10)  |
| Volume/Å³           | 4091.26(14) | 8976.0(4)    | 4322.4(8)    |
| Z                   | 4           | 8            | 2            |
| ρ\_calc/g/cm³       | 1.803       | 1.694        | 1.752        |
| μ/mm\(^1\)         | 2.411       | 2.191        | 2.322        |
| F(000)              | 2180        | 4552         | 2252         |
| Crystal size/mm³    | 0.23 × 0.20 × 0.17 | 0.31 × 0.23 × 0.16 | 0.10 × 0.07 × 0.05 |
| Radiation           | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 5.8 to 50.1 | 6.46 to 50.08 | 5.76 to 50.12 |
| Index ranges        | -11 ≤ h ≤ 11, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24 | -41 ≤ h ≤ 42, -13 ≤ k ≤ 13, -27 ≤ l ≤ 26 | -18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23 |
| Reflections collected | 53081       | 32816        | 34536        |
| Independent reflections | 7217 [R\_int = 0.0745] | 7932 [R\_int = 0.0414] | 15245 [R\_int = 0.1551] |
| Data/restraints/parameters | 7217/0/534 | 7932/0/563 | 15245/0/583 |
| Goodness-of-fit on F\(^2\) | 1.158       | 1.101        | 0.965        |
| Final R indexes [I≥2σ (I)] | R\(_1\) = 0.0582, wR\(_2\) = 0.1068 | R\(_1\) = 0.0276, wR\(_2\) = 0.0527 | R\(_1\) = 0.0963, wR\(_2\) = 0.1632 |
| Final R indexes [all data] | R\(_1\) = 0.0924, wR\(_2\) = 0.1283 | R\(_1\) = 0.0364, wR\(_2\) = 0.0580 | R\(_1\) = 0.2156, wR\(_2\) = 0.2540 |
| Largest diff. peak/hole / e Å\(^3\) | 2.83/-1.47 | 0.72/-0.66 | 3.56/-1.46 |
**Table SI2:** Bond Lengths for (3).

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Dy1  | Na1\(^1\) | 3.324(3) | C26  | C27  | 1.345(12) |
| Dy1  | N11  | 2.531(7) | C27  | C28  | 1.388(12) |
| Dy1  | O12  | 2.318(6) | Cl28 | C28  | 1.388(12) |
| Dy1  | O19  | 2.323(5) | C28  | C29  | 1.388(12) |
| Dy1  | N21  | 2.591(6) | O29  | C29  | 1.452(11) |
| Dy1  | O29  | 2.319(6) | C29  | C30  | 1.329(10) |
| Dy1  | N31  | 2.547(7) | N31  | C32  | 1.329(10) |
| Dy1  | O39  | 2.282(5) | N31  | C40  | 1.435(11) |
| Na1  | O12\(^1\) | 2.308(7) | C32  | C33  | 1.420(12) |
| Na1  | O19\(^1\) | 2.375(6) | C33  | C34  | 1.366(12) |
| Na1  | Cl28\(^1\) | 3.018(4) | C34  | C35  | 1.406(12) |
| Na1  | O29\(^1\) | 2.307(6) | C35  | C36  | 1.420(12) |
| Na1  | O100 | 2.175(8) | C36  | C37  | 1.754(8)  |
| N11  | C12  | 1.322(10)| C36  | C37  | 1.365(12) |
| N11  | C20  | 1.380(10)| C37  | C38  | 1.402(12) |
| O12  | C49  | 1.288(10)| Cl38 | C38  | 1.738(8)  |
| Cl12 | C13  | 1.423(12)| C38  | C39  | 1.396(11) |
| C13  | C14  | 1.380(12)| O39  | C39  | 1.292(9)  |
| C14  | C15  | 1.404(12)| C39  | C40  | 1.422(12) |
| C15  | C16  | 1.421(12)| N41  | C42  | 1.323(11) |
| C15  | C20  | 1.424(11)| N41  | C50  | 1.398(10) |
| Cl16 | C16  | 1.753(9) | C42  | C43  | 1.394(12) |
| C16  | C17  | 1.367(13)| C43  | C44  | 1.420(13) |
| C17  | C18  | 1.392(12)| C44  | C45  | 1.397(12) |
| Cl18 | C18  | 1.743(9) | C45  | C46  | 1.426(11) |
| C18  | C19  | 1.403(11)| C45  | C50  | 1.413(11) |
| O19  | C19  | 1.303(9) | Cl46 | C46  | 1.734(8)  |
| C19  | C20  | 1.442(12)| C46  | C47  | 1.393(12) |
| N21  | C22  | 1.340(10)| C47  | C48  | 1.392(12) |
| N21  | C30  | 1.375(10)| Cl48 | C48  | 1.741(9)  |
| C22  | C23  | 1.405(12)| C48  | C49  | 1.399(11) |
| C23  | C24  | 1.360(12)| C49  | C50  | 1.426(12) |
| C24  | C25  | 1.422(12)| O100 | C103 | 1.251(13) |
| C25  | C26  | 1.396(12)| N100 | C101 | 1.462(13) |
| C25  | C30  | 1.409(11)| N100 | C102 | 1.436(14) |
| Cl26 | C26  | 1.754(9) | N100 | C103 | 1.321(13) |

\(^1\)1-X,1-Y,2-Z
\textit{Table SI3: Bond Angles for (3).}

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N11  | Dy1  | Na1$^1$ | 94.15(16) | C15  | C20  | C19  | 122.5(7) |
| N11  | Dy1  | N21   | 156.1(2)  | C22  | N21  | Dy1  | 129.2(6) |
| N11  | Dy1  | N31   | 93.7(2)   | C22  | N21  | C30  | 117.6(7) |
| N11  | Dy1  | N41   | 79.6(2)   | C30  | N21  | Dy1  | 112.0(5) |
| O12  | Dy1  | Na1$^1$ | 43.95(16) | N21  | C22  | C23  | 122.6(8) |
| O12  | Dy1  | N11   | 80.7(2)   | C24  | C23  | C22  | 120.2(8) |
| O12  | Dy1  | O19   | 77.0(2)   | C23  | C24  | C25  | 119.3(8) |
| O12  | Dy1  | N21   | 107.5(2)  | C26  | C25  | C24  | 125.0(8) |
| O12  | Dy1  | O29   | 72.5(2)   | C26  | C25  | C30  | 117.7(8) |
| O12  | Dy1  | N31   | 150.5(2)  | C30  | C25  | C24  | 117.2(8) |
| O12  | Dy1  | N41   | 66.5(2)   | C25  | C26  | Cl26 | 119.7(7) |
| O19  | Dy1  | Na1$^1$ | 45.61(15) | C27  | C26  | C25  | 120.2(8) |
| O19  | Dy1  | N11   | 67.3(2)   | C27  | C26  | Cl26 | 120.1(7) |
| O19  | Dy1  | N21   | 135.8(2)  | C26  | C27  | C28  | 122.6(9) |
| O19  | Dy1  | N31   | 74.2(2)   | C28  | Cl28 | Na1$^1$ | 94.9(3) |
| O19  | Dy1  | N41   | 134.0(2)  | C27  | C28  | Cl28 | 120.2(7) |
| N21  | Dy1  | Na1$^1$ | 107.31(16)| C29  | C28  | C27  | 121.7(8) |
| O29  | Dy1  | Na1$^1$ | 43.93(15) | C29  | C28  | Cl28 | 118.0(7) |
| O29  | Dy1  | N11   | 137.4(2)  | Na1$^1$ | O29  | Dy1  | 91.9(2) |
| O29  | Dy1  | O19   | 74.61(19) | C29  | O29  | Dy1  | 120.3(5) |
| O29  | Dy1  | N21   | 65.8(2)   | C29  | O29  | Na1$^1$ | 126.6(5) |
| O29  | Dy1  | N31   | 93.8(2)   | C28  | C29  | C30  | 114.6(7) |
| O29  | Dy1  | N41   | 117.0(2)  | O29  | C29  | C28  | 125.3(8) |
| N31  | Dy1  | Na1$^1$ | 108.52(16)| O29  | C29  | C30  | 120.0(8) |
| N31  | Dy1  | N21   | 89.3(2)   | N21  | C30  | C25  | 122.9(7) |
| N31  | Dy1  | N41   | 141.2(2)  | N21  | C30  | C29  | 114.6(7) |
| O39  | Dy1  | Na1$^1$ | 174.80(15)| C25  | C30  | C29  | 122.5(8) |
| O39  | Dy1  | N11   | 84.0(2)   | C32  | N31  | Dy1  | 128.5(5) |
| O39  | Dy1  | O12   | 140.0(2)  | C32  | N31  | C40  | 118.4(7) |
| O39  | Dy1  | O19   | 129.40(19)| C40  | N31  | Dy1  | 112.3(5) |
| O39  | Dy1  | N21   | 75.5(2)   | N31  | C32  | C33  | 123.8(8) |
| O39  | Dy1  | O29   | 136.9(2)  | C34  | C33  | C32  | 117.8(8) |
| O39  | Dy1  | N31   | 66.8(2)   | C33  | C34  | C35  | 120.9(8) |
| O39  | Dy1  | N41   | 74.5(2)   | C34  | C35  | C36  | 126.6(8) |
| N41  | Dy1  | Na1$^1$ | 110.02(17)| C34  | C35  | C40  | 117.7(8) |
| N41  | Dy1  | N21   | 83.3(2)   | C36  | C35  | C40  | 115.7(8) |
| O12$^1$ | Na1  | Dy1$^1$ | 44.20(15)| C35  | C36  | Cl36 | 118.5(7) |
| O12$^1$ | Na1  | O19$^1$ | 76.2(2)   | C37  | C36  | C35  | 122.5(8) |
| O12$^1$ | Na1  | Cl28$^1$ | 107.2(2)  | C37  | C36  | Cl36 | 119.0(6) |
| O19$^1$ | Na1  | Dy1$^1$ | 44.34(14) | C36  | C37  | C38  | 119.7(8) |
| O19$^1$ | Na1  | Cl28$^1$ | 137.1(2)  | C37  | C38  | Cl38 | 118.6(6) |
### Table SI4: Bond Lengths for (4).

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Dy1  | N11  | 2.577(3) | N31  | C32  | 1.325(4) |
| Dy1  | O19  | 2.295(2) | N31  | C40  | 1.364(4) |
| Dy1  | N21  | 2.634(2) | C32  | C33  | 1.403(4) |
| Dy1  | O29  | 2.269(2) | C33  | C34  | 1.364(5) |
| Dy1  | N31  | 2.672(3) | C34  | C35  | 1.417(4) |
| Dy1  | O39  | 2.287(2) | C35  | C36  | 1.420(5) |
| Dy1  | N41  | 2.519(2) | C35  | C40  | 1.425(4) |
| Dy1  | O49  | 2.292(2) | C36  | Cl36 | 1.751(3) |
| N11  | C12  | 1.326(4) | C36  | C37  | 1.355(4) |
| N11  | C20  | 1.375(4) | C37  | C38  | 1.410(4) |
| C12  | C13  | 1.427(4) | C38  | Cl38 | 1.742(3) |
| C13  | C14  | 1.359(4) | C38  | C39  | 1.390(4) |
| C14  | C15  | 1.416(4) | O39  | C39  | 1.299(3) |
| C15  | C16  | 1.420(4) | C39  | C40  | 1.446(4) |
| C15  | C20  | 1.421(4) | N41  | C42  | 1.331(4) |
| C16  | Cl16 | 1.748(3) | N41  | C50  | 1.365(4) |
| C16  | C17  | 1.360(4) | C42  | C43  | 1.394(4) |
| C17  | C18  | 1.400(4) | C43  | C44  | 1.370(4) |
| C18  | Cl18 | 1.746(3) | C44  | C45  | 1.405(4) |
| C18  | C19  | 1.397(4) | C45  | C46  | 1.413(4) |
| O19  | C19  | 1.297(4) | C45  | C50  | 1.414(4) |
| C19  | C20  | 1.444(4) | C46  | Cl46 | 1.743(3) |
| N21  | C22  | 1.325(4) | C46  | C47  | 1.365(4) |
| N21  | C30  | 1.379(4) | C47  | C48  | 1.408(4) |
| C22  | C23  | 1.410(4) | C48  | Cl48 | 1.745(3) |
| C23  | C24  | 1.366(4) | C48  | C49  | 1.390(4) |
| C24  | C25  | 1.410(4) | O49  | C49  | 1.302(3) |
| C25  | C26  | 1.417(4) | C49  | C50  | 1.457(4) |
| C25  | C30  | 1.427(4) | N100 | C101 | 1.522(4) |
| C26  | Cl26 | 1.750(3) | N100 | C111 | 1.519(4) |
| C26  | C27  | 1.365(4) | N100 | C121 | 1.520(4) |
| C27  | C28  | 1.403(4) | N100 | C131 | 1.514(4) |
| C28  | Cl28 | 1.742(3) | C101 | C102 | 1.511(4) |
| C28  | C29  | 1.387(4) | C111 | C112 | 1.510(5) |
| O29  | C29  | 1.298(3) | C121 | C122 | 1.519(4) |
| C29  | C30  | 1.434(4) | C131 | C132 | 1.516(5) |
Table S15: Bond Angles for (4).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N11  | Dy1  | N21  | 138.40(8) | C29  | C28  | C27  | 123.1(3) |
| N11  | Dy1  | N31  | 73.50(8)  | C29  | C28  | Cl28 | 117.1(2) |
| O19  | Dy1  | N11  | 66.17(8)  | C29  | O29  | Dy1  | 125.75(19) |
| O19  | Dy1  | N21  | 153.88(8) | C28  | C29  | C30  | 115.4(3) |
| O19  | Dy1  | N31  | 87.46(7)  | O29  | C29  | C28  | 124.0(3) |
| O19  | Dy1  | N41  | 79.46(8)  | O29  | C29  | C30  | 120.5(3) |
| N21  | Dy1  | N31  | 106.58(7) | N21  | C30  | C25  | 122.0(3) |
| O29  | Dy1  | N11  | 74.10(8)  | N21  | C30  | C29  | 115.3(3) |
| O29  | Dy1  | O19  | 139.94(7) | C25  | C30  | C29  | 122.8(3) |
| O29  | Dy1  | N21  | 65.95(7)  | C30  | C31  | N31  | 129.4(2) |
| O29  | Dy1  | O39  | 114.53(7) | C40  | N31  | Dy1  | 112.8(2) |
| O29  | Dy1  | N41  | 136.18(7) | N31  | C32  | C33  | 123.9(3) |
| O29  | Dy1  | O49  | 85.37(7)  | C32  | N31  | C40  | 118.8(3) |
| O39  | Dy1  | N11  | 132.19(8) | C33  | C34  | C35  | 120.2(3) |
| O39  | Dy1  | O19  | 89.64(7)  | C34  | C35  | C36  | 125.9(3) |
| O39  | Dy1  | N21  | 77.44(7)  | C34  | C35  | C40  | 116.5(3) |
| O39  | Dy1  | N31  | 64.42(8)  | C34  | C35  | C40  | 117.6(3) |
| O39  | Dy1  | N41  | 73.80(8)  | C34  | C35  | Cl36 | 119.6(3) |
| O39  | Dy1  | O49  | 138.48(7) | C37  | C36  | C35  | 121.4(3) |
| N41  | Dy1  | N11  | 134.15(8) | C37  | C36  | Cl36 | 119.0(3) |
| N41  | Dy1  | N21  | 75.18(8)  | C36  | C37  | C38  | 120.2(3) |
| N41  | Dy1  | N31  | 136.19(8) | C37  | C38  | Cl38 | 119.0(3) |
| O49  | Dy1  | N11  | 87.12(7)  | C39  | C38  | C37  | 123.1(3) |
| O49  | Dy1  | O19  | 97.27(7)  | C39  | C38  | Cl38 | 117.9(3) |
| O49  | Dy1  | N21  | 78.82(7)  | C39  | O39  | Dy1  | 126.72(19) |
| O49  | Dy1  | N31  | 156.28(7) | C38  | C39  | C40  | 115.7(3) |
| O49  | Dy1  | N41  | 67.44(7)  | O39  | C39  | C38  | 125.0(3) |
| C12  | N11  | Dy1  | 127.8(2)  | O39  | C39  | C40  | 119.3(3) |
| C12  | N11  | C20  | 117.7(3)  | N31  | C40  | C35  | 122.8(3) |
| C20  | N11  | Dy1  | 112.94(19)| N31  | C40  | C39  | 115.1(3) |
| N11  | C12  | C13  | 124.1(3)  | C35  | C40  | C39  | 122.0(3) |
| C14  | C13  | C12  | 117.7(3)  | C42  | N41  | Dy1  | 127.4(2) |
| C13  | C14  | C15  | 121.1(3)  | C42  | N41  | C50  | 117.8(3) |
| C14  | C15  | C16  | 125.9(3)  | C50  | N41  | Dy1  | 114.77(19) |
| C14  | C15  | C20  | 117.0(3)  | N41  | C42  | C43  | 123.8(3) |
| C16  | C15  | C20  | 117.1(3)  | C44  | C43  | C42  | 118.6(3) |
| C15  | C16  | C16  | 118.8(3)  | C43  | C44  | C45  | 120.2(3) |
| C17  | C16  | C15  | 121.3(3)  | C44  | C45  | C46  | 125.1(3) |
| C17  | C16  | Cl16 | 119.9(3)  | C44  | C45  | C50  | 117.3(3) |
| C16  | C17  | C18  | 120.4(3)  | C46  | C45  | C50  | 117.6(3) |
| Atom   | Atom   | Length/Å   | Atom   | Length/Å   |
|--------|--------|------------|--------|------------|
| Dy1    | N11    | 2.525(10)  | O49    | 1.300(15)  |
| Dy1    | O19    | 2.305(9)   | O49    | 3.048(11)  |
| Dy1    | N21    | 2.559(12)  | C49    | 1.451(19)  |
| Dy1    | O29    | 2.318(11)  | N51    | 1.321(19)  |
| Dy1    | N31    | 2.537(11)  | N51    | 1.389(16)  |
| Dy1    | O39    | 2.314(9)   | C52    | 1.39(2)    |
| Dy1    | N41    | 2.601(12)  | C53    | 1.376(19)  |
| Dy1    | O49    | 2.275(9)   | C54    | 1.39(2)    |
| Dy1    | K1<sup>1</sup> | 3.9634(9) | C55    | 1.413(18)  |
| Dy2    | N51    | 2.532(13)  | C55    | 1.427(19)  |
| Dy2    | O59    | 2.325(9)   | C56    | 1.748(16)  |
| Dy2    | N61    | 2.550(11)  | C56    | 1.37(2)    |

<sup>1</sup>At the single-crystal X-ray measurement.

**Table SI6:** Bond Lengths for (5).
Table SI7: Bond Angles for (5).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| N11  | Dy1  | N21  | 93.8(3) | C67  | C68  | C168 | 118.9(13) |
| N11  | Dy1  | N31  | 95.9(3) | C67  | C68  | C69  | 122.1(14) |
| N11  | Dy1  | N41  | 142.7(4) | C69  | C68  | C168 | 118.9(11) |
| N11  | Dy1  | K11  | 100.5(3) | C68  | C168 | K2   | 95.6(5)   |
| O19  | Dy1  | N11  | 67.2(4) | Dy2  | O69  | K2   | 98.9(3)   |
| O19  | Dy1  | N21  | 74.1(4) | C69  | O69  | Dy2  | 122.8(9) |
| O19  | Dy1  | O29  | 125.2(3) | C69  | O69  | K2   | 125.8(8) |
| O19  | Dy1  | N31  | 81.8(4) | C68  | C69  | C70  | 116.2(12) |
| O19  | Dy1  | O39  | 128.7(3) | O69  | C69  | C68  | 123.2(13) |
| O19  | Dy1  | N41  | 75.5(4) | O69  | C69  | C70  | 120.6(13) |
| O19  | Dy1  | K11  | 166.8(3) | N61  | C70  | C65  | 125.6(14) |
| N21  | Dy1  | N41  | 76.2(4) | N61  | C70  | C69  | 113.1(12) |
| N21  | Dy1  | K11  | 103.0(3) | C65  | C70  | C69  | 121.2(14) |

1+X,-1+Y,+Z
|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| O29 | Dy1 | N11 | 79.5(3) | C72 | N71 | Dy2 | 127.7(11) |
| O29 | Dy1 | N21 | 65.9(4) | C72 | N71 | C80 | 120.4(14) |
| O29 | Dy1 | N31 | 145.9(4) | C80 | N71 | Dy2 | 111.8(9) |
| O29 | Dy1 | N41 | 125.4(3) | N71 | C72 | C73 | 122.4(15) |
| O29 | Dy1 | K1₁ | 44.4(2) | C74 | C73 | C72 | 118.5(15) |
| N31 | Dy1 | N21 | 148.1(4) | C73 | C74 | C75 | 119.2(17) |
| N31 | Dy1 | N41 | 77.7(4) | C74 | C75 | C76 | 122.7(16) |
| N31 | Dy1 | K1₁ | 105.0(3) | C80 | C75 | C74 | 119.7(15) |
| O39 | Dy1 | N11 | 76.1(3) | C80 | C75 | C76 | 117.4(14) |
| O39 | Dy1 | N21 | 144.7(4) | C75 | C76 | C76 | 120.7(13) |
| O39 | Dy1 | O29 | 79.0(3) | C77 | C76 | C75 | 118.1(17) |
| O39 | Dy1 | N31 | 67.3(4) | C77 | C76 | C76 | 121.0(13) |
| O39 | Dy1 | N41 | 130.9(4) | C76 | C77 | C78 | 122.0(16) |
| O39 | Dy1 | K1₁ | 48.0(2) | C77 | C78 | C78 | 117.6(13) |
| N41 | Dy1 | K1₁ | 116.7(3) | C79 | C78 | C77 | 121.5(16) |
| O49 | Dy1 | N11 | 150.4(4) | C79 | C78 | C78 | 120.7(14) |
| O49 | Dy1 | O19 | 142.3(4) | Dy2 | O79 | K2 | 90.2(3) |
| O49 | Dy1 | N21 | 94.5(3) | C79 | O79 | Dy2 | 122.2(9) |
| O49 | Dy1 | O29 | 78.3(3) | C79 | O79 | K2 | 147.3(9) |
| O49 | Dy1 | N31 | 91.8(3) | C78 | C79 | C80 | 116.4(16) |
| O49 | Dy1 | O39 | 80.7(3) | O79 | C79 | C78 | 120.9(15) |
| O49 | Dy1 | N41 | 66.8(4) | O79 | C79 | C80 | 122.6(14) |
| O49 | Dy1 | K1₁ | 50.0(3) | N71 | C80 | C75 | 119.5(14) |
| N51 | Dy2 | N61 | 99.6(4) | N71 | C80 | C79 | 116.0(15) |
| N51 | Dy2 | N71 | 142.7(4) | C79 | C80 | C75 | 124.4(15) |
| N51 | Dy2 | N81 | 89.5(4) | C82 | N81 | Dy2 | 127.5(9) |
| N51 | Dy2 | K2 | 95.6(3) | C82 | N81 | C90 | 118.2(12) |
| O59 | Dy2 | N51 | 67.1(4) | C90 | N81 | Dy2 | 114.2(9) |
| O59 | Dy2 | N61 | 84.0(3) | N81 | C82 | C83 | 125.7(13) |
| O59 | Dy2 | N71 | 75.6(4) | C82 | C83 | C84 | 119.2(15) |
| O59 | Dy2 | N81 | 72.0(3) | C83 | C84 | C85 | 117.1(14) |
| O59 | Dy2 | O89 | 125.7(3) | C84 | C85 | C86 | 124.0(14) |
| O59 | Dy2 | K2 | 162.3(2) | C84 | C85 | C90 | 120.3(13) |
| N61 | Dy2 | N71 | 76.2(4) | C90 | C85 | C86 | 115.7(14) |
| N61 | Dy2 | N81 | 148.6(4) | C85 | C86 | C86 | 117.7(11) |
| N61 | Dy2 | K2 | 102.9(3) | C87 | C86 | C85 | 120.0(13) |
| O69 | Dy2 | N51 | 74.7(4) | C87 | C86 | C86 | 122.2(10) |
| O69 | Dy2 | O59 | 126.4(3) | C86 | C87 | C88 | 121.7(13) |
| O69 | Dy2 | N61 | 66.6(4) | C87 | C88 | C88 | 119.3(11) |
| O69 | Dy2 | N71 | 132.2(4) | C89 | C88 | C87 | 122.1(14) |
| O69 | Dy2 | N81 | 144.5(3) | C89 | C88 | C88 | 118.3(11) |
| O69 | Dy2 | O89 | 79.9(3) | C88 | C88 | K2 | 100.2(5) |
| O69 | Dy2 | K2 | 46.3(2) | Dy2 | O89 | K2 | 101.5(3) |
N71  Dy2  K2  121.7(3)  C89  O89  Dy2  123.7(9)
O79  Dy2  N51  149.9(4)  C89  O89  K2  132.1(8)
O79  Dy2  O59  142.9(4)  C88  C89  C90  115.6(13)
O79  Dy2  N61  84.7(3)  O89  C89  C88  124.4(13)
O79  Dy2  O69  79.9(4)  O89  C89  C90  119.6(12)
O79  Dy2  N71  67.3(4)  N81  C90  C85  119.2(14)
O79  Dy2  N81  102.3(3)  N81  C90  C89  115.9(13)
O79  Dy2  O89  80.2(3)  C89  C90  C85  124.4(13)
O79  Dy2  K2  54.7(3)  Dy1²  K1  Dy1³  180.0
N81  Dy2  N71  78.4(4)  Cl28²  K1  Dy1²  91.40(7)
O89  Dy2  K2  106.1(2)  Cl28³  K1  Dy1²  88.60(7)
O89  Dy2  N51  79.7(4)  Cl28³  K1  Dy1³  91.40(7)
O89  Dy2  N61  145.2(4)  Cl28²  K1  Dy1³  88.60(7)
O89  Dy2  N71  124.6(3)  Cl28³  K1  Cl28²  180.0
O89  Dy2  N81  65.9(3)  Cl28³  K1  Cl48²  60.55(9)
O89  Dy2  K2  43.4(2)  Cl28²  K1  Cl48²  119.45(9)
C12  N11  Dy1  127.5(10)  Cl28³  K1  Cl48³  119.45(9)
C12  N11  C20  119.3(13)  Cl28²  K1  Cl48³  60.55(9)
C20  N11  Dy1  112.7(9)  O29³  K1  Dy1²  144.9(2)
N11  C12  C13  122.2(15)  O29³  K1  Dy1³  35.1(2)
C14  C13  C12  120.6(16)  O29²  K1  Dy1³  144.9(2)
C13  C14  C15  120.2(15)  O29²  K1  Dy1²  35.1(2)
C14  C15  C16  126.3(14)  O29³  K1  Cl28³  56.3(2)
C14  C15  C20  117.7(15)  O29²  K1  Cl28²  56.3(2)
C20  C15  C16  116.0(15)  O29²  K1  Cl28³  123.7(2)
C15  C16  C16  120.4(12)  O29³  K1  Cl28²  123.7(2)
C17  C16  C15  119.7(14)  O29²  K1  O29³  180.0
C17  C16  C16  119.9(12)  O29²  K1  O39²  61.1(3)
C16  C17  C18  122.5(15)  O29³  K1  O39²  118.9(3)
C17  C18  C18  120.2(12)  O29³  K1  O39³  61.1(3)
C17  C18  C19  123.5(15)  O29²  K1  O39³  118.9(3)
C19  C18  C18  116.3(11)  O29²  K1  Cl48²  101.9(2)
C19  O19  Dy1  121.2(10)  O29²  K1  Cl48³  78.1(2)
C18  C19  C20  112.7(14)  O29³  K1  Cl48²  78.1(2)
O19  C19  C18  126.8(15)  O29³  K1  Cl48³  101.9(2)
O19  C19  C20  120.5(14)  O29³  K1  O49²  121.0(3)
N11  C20  C15  119.6(15)  O29³  K1  O49³  121.0(3)
N11  C20  C19  114.8(13)  O29²  K1  O49²  59.0(3)
C15  C20  C19  125.6(15)  O29³  K1  O49³  59.0(3)
C22  N21  Dy1  125.8(11)  O39²  K1  Dy1²  35.46(18)
C22  N21  C30  119.8(13)  O39³  K1  Dy1³  35.46(18)
C30  N21  Dy1  114.2(10)  O39³  K1  Dy1²  144.54(18)
N21  C22  C23  125.4(15)  O39²  K1  Dy1³  144.54(18)
| C24  | C23  | C22  | 112.8(16) | O39 | K1   | Cl28 | 108.7(2) |
|------|------|------|-----------|-----|------|------|----------|
| C25  | C24  | C23  | 123.2(15) | O39 | K1   | Cl28 | 71.3(2)  |
| C24  | C25  | C26  | 124.5(15) | O39 | K1   | Cl28 | 108.7(2) |
| C24  | C25  | C30  | 118.1(16) | O39 | K1   | Cl28 | 71.3(2)  |
| C26  | C25  | C30  | 117.3(16) | O39 | K1   | O39  | 180.0    |
| C25  | C26  | Cl26 | 119.4(13) | O39 | K1   | Cl48 | 103.1(2) |
| C27  | C26  | C25  | 120.9(15) | O39 | K1   | Cl48 | 76.9(2)  |
| C27  | C26  | Cl26 | 119.6(13) | O39 | K1   | Cl48 | 76.9(2)  |
| C26  | C27  | C28  | 121.0(17) | O39 | K1   | Cl48 | 103.1(2) |
| C27  | C28  | Cl28 | 120.7(13) | O39 | K1   | O49  | 59.2(2)  |
| C27  | C28  | C29  | 121.5(16) | O39 | K1   | O49  | 120.8(2) |
| C29  | C28  | Cl28 | 117.7(11) | O39 | K1   | O49  | 120.8(2) |
| C28  | Cl28 | K1   | 95.9(5)   | O39 | K1   | O49  | 59.2(2)  |
| Dy1  | O29  | K1   | 100.5(3)  | Cl48 | K1   | Dy1  | 93.99(7) |
| C29  | O29  | Dy1  | 122.3(10) | Cl48 | K1   | Dy1  | 86.01(7) |
| C29  | O29  | K1   | 120.4(8)  | Cl48 | K1   | Dy1  | 93.99(7) |
| O29  | C29  | C28  | 123.5(15) | Cl48 | K1   | Dy1  | 86.01(7) |
| O29  | C29  | C30  | 120.8(15) | Cl48 | K1   | Cl48 | 180.0    |
| C30  | C29  | C28  | 115.7(13) | O49 | K1   | Dy1  | 145.14(16) |
| N21  | C30  | C25  | 120.6(16) | O49 | K1   | Dy1  | 34.86(16) |
| N21  | C30  | C29  | 115.9(14) | O49 | K1   | Dy1  | 34.86(16) |
| C29  | C30  | C25  | 123.5(16) | O49 | K1   | Dy1  | 145.14(16) |
| C32  | N31  | Dy1  | 128.9(10) | O49 | K1   | Cl28 | 108.14(19) |
| C32  | N31  | C40  | 116.8(13) | O49 | K1   | Cl28 | 108.14(19) |
| C40  | N31  | Dy1  | 114.2(9) | O49 | K1   | Cl28 | 71.86(19) |
| N31  | C32  | C33  | 126.6(15) | O49 | K1   | Cl28 | 71.86(19) |
| C34  | C33  | C32  | 115.8(16) | O49 | K1   | Cl48 | 51.16(17) |
| C33  | C34  | C35  | 120.9(16) | O49 | K1   | Cl48 | 51.16(17) |
| C34  | C35  | C36  | 123.7(15) | O49 | K1   | Cl48 | 128.84(17) |
| C34  | C35  | C40  | 118.1(15) | O49 | K1   | Cl48 | 128.84(17) |
| C40  | C35  | C36  | 118.1(16) | O49 | K1   | O49  | 180.0    |
| C35  | C36  | Cl36 | 119.4(13) | Dy2  | K2   | Dy2  | 180.0    |
| C37  | C36  | C35  | 119.7(15) | Cl68 | K2   | Dy2  | 86.73(6) |
| C37  | C36  | Cl36 | 120.9(12) | Cl68 | K2   | Dy2  | 93.27(6) |
| C36  | C37  | C38  | 119.5(15) | Cl68 | K2   | Dy2  | 93.27(6) |
| C37  | C38  | Cl38 | 117.3(12) | Cl68 | K2   | Dy2  | 86.73(6) |
| C39  | C38  | C37  | 125.4(16) | Cl68 | K2   | Cl68 | 180.00(10) |
| C39  | C38  | Cl38 | 117.1(12) | O69  | K2   | Dy2  | 145.17(19) |
| C38  | C39  | C40  | 113.9(13) | O69  | K2   | Dy2  | 34.83(19) |
| O39  | C39  | C38  | 125.3(15) | O69  | K2   | Dy2  | 145.17(19) |
| O39  | C39  | C40  | 120.7(14) | O69  | K2   | Dy2  | 34.83(19) |
| Dy1  | O39  | K1   | 96.5(3)  | O69  | K2   | Cl68 | 127.8(2) |
| C39  | O39  | Dy1  | 122.5(10) | O69  | K2   | Cl68 | 127.8(2) |
C39 O39 K1 123.8(8) O69 K2 Cl68 52.2(2)
N31 C40 C35 121.7(14) O69 K2 Cl68 K1 52.2(2)
N31 C40 C39 115.2(13) O69 K2 O69 180.0
C35 C40 C39 123.1(14) O69 K2 O79 56.8(3)
C42 N41 Dy1 128.6(9) O69 K2 O79 56.8(3)
C42 N41 C50 117.8(13) O69 K2 O79 123.2(3)
C50 N41 Dy1 113.4(10) O69 K2 O79 123.2(3)
N41 C42 C43 125.6(14) O69 K2 Cl88 108.97(19)
C44 C43 C42 117.2(15) O69 K2 Cl88 71.03(19)
C45 C44 C43 120.8(14) O69 K2 Cl88 71.03(19)
C44 C45 C46 127.8(14) O69 K2 Cl88 108.97(19)
C44 C45 C50 117.9(13) O79 K2 Dy2 144.93(17)
C46 C45 C50 114.3(14) O79 K2 Dy2 35.07(17)
C45 C46 Cl46 118.3(13) O79 K2 Dy2 35.07(17)
C47 C46 C45 123.3(15) O79 K2 Dy2 144.93(17)
C47 C46 Cl46 118.4(11) O79 K2 Cl68 76.66(17)
C48 C47 C46 119.0(13) O79 K2 Cl68 103.34(17)
C47 C48 Cl48 118.2(10) O79 K2 Cl68 76.66(17)
C47 C48 C49 125.1(14) O79 K2 Cl68 103.34(17)
C49 C48 Cl48 116.6(11) O79 K2 O79 180.0(4)
C48 Cl48 K1 106.0(4) O79 K2 Cl88 70.95(18)
Dy1 O49 K1 95.2(3) O79 K2 Cl88 109.05(18)
C49 O49 Dy1 123.8(9) O79 K2 Cl88 109.05(18)
C49 O49 K1 140.3(8) O79 K2 Cl88 70.95(18)
C48 C49 C50 113.0(13) Cl88 K2 Dy2 90.49(6)
O49 C49 C48 125.3(14) Cl88 K2 Dy2 90.49(6)
O49 C49 C50 121.6(12) Cl88 K2 Dy2 89.51(6)
N41 C50 C45 120.6(14) Cl88 K2 Dy2 89.51(6)
N41 C50 C49 114.2(13) Cl88 K2 Cl68 62.72(10)
C45 C50 C49 125.2(12) Cl88 K2 Cl68 62.72(10)
C52 N51 Dy2 127.9(11) Cl88 K2 Cl68 117.28(10)
C52 N51 C60 117.5(14) Cl88 K2 Cl68 117.28(10)
C60 N51 Dy2 114.2(10) Cl88 K2 Cl68 180.0
N51 C52 C53 122.4(16) O89 K2 Dy2 144.93(18)
C54 C53 C52 120.2(18) O89 K2 Dy2 144.93(18)
C53 C54 C55 120.6(17) O89 K2 Dy2 35.07(18)
C54 C55 C56 126.5(15) O89 K2 Dy2 35.07(18)
C54 C55 C60 115.4(14) O89 K2 Cl68 73.8(2)
C56 C55 C60 118.0(14) O89 K2 Cl68 73.8(2)
C55 C56 Cl56 119.3(12) O89 K2 Cl68 106.2(2)
C57 C56 C55 120.1(15) O89 K2 Cl68 106.2(2)
C57 C56 Cl56 120.6(12) O89 K2 O69 117.1(3)
C56 C57 C58 121.8(15) O89 K2 O69 62.9(3)
Interestingly, NaDyClq (3) and K0.5(NEt4)0.5DyClq (5) have a similar coordination sphere, but NEtDyClq (4) is different since the ligands have a different arrangement around the lanthanide center.
2. IR spectra

The IR spectra of the powdered compounds are compared with the films finding an excellent agreement. The characteristic vibration modes of the molecules place in the range \([1700 - 500]\) \(\text{cm}^{-1}\). The bands in the range \([1600 - 1300]\) \(\text{cm}^{-1}\) are mainly attributed to \(\text{C} = \text{N}\) and \(\text{C} = \text{C}\) vibration frequencies (ring stretching) while the band at \(1100\) \(\text{cm}^{-1}\) is related to the \(\text{CO}\) stretching. The \(\text{C} - \text{Cl}\) vibration locates in the range \([958 - 954]\) \(\text{cm}^{-1}\).

Fig. SI3: IR transmission spectra for the bulk compounds, \(\text{NaYClq}\) (1), \(\text{NaTbClq}\) (2), \(\text{NaDyClq}\) (3), \(\text{NEtDyClq}\) (4) and \(\text{KNEtDyClq}\) (5), compared with the deposited films where the ligand vibrations can be detected.
3. Mass Spectrometry

Electrospray ionization mass spectrometry (ESI-MS) has been performed for all bulk compounds. For the five cases the main signal corresponds to the relation mass/charge (m/z) of the ionized molecule: \([\text{Dy}[(5,7\text{Cl}_2\text{q}_4)]^-\). On the right hand side of the figure the pattern of the main signal is compared to the theoretical pattern, matching in all cases. The secondary signals are attributed to fragmentations of the molecules caused by the technique itself.
**Fig. SI4**: Electrospray ionization mass spectrometry (ESI-MS) for the bulk compounds, a-b (1), c-d (2), e-f (3), g-h (4) and i-j (5), in negative mode.
4. Radial Effective Charge (REC) model

Let us start with a caveat: it has been recently pointed out, both experimentally and via theoretical calculations, that spin-vibration coupling are critical for relaxation processes\textsuperscript{3–5}, meaning the nature of the ground state and the apparent energy barrier are not sufficient conditions to predict SMM behaviour. Despite early successes, currently the necessary theory to fully understand these spin-vibrational-governed relaxation processes is still being developed.

Moreover, even state-of-the-art models for determining the energy level scheme of the magnetic levels, which are much more mature, have important limitations. This has been recently studied with a benchmark study\textsuperscript{6} With that being said, one of said state-of-the-art models is the Radial Effective Charge (REC) model, so we apply it here to verify a high-spin ground state, separated by a non-negligible energy from the first excited states as indications for a potential SMM behaviour.

Our calculations start with the crystallographic/non-idealized atomic coordinates of the first coordination sphere. These are introduced as an input for the portable fortran77 software code SIMPRE\textsuperscript{7}. This code parameterizes the electric field effect produced by the surrounding ligands, acting over the central ion, by using the following Crystal Field (CF) Hamiltonian expressed in terms of the Extended Stevens Operators (ESOs)\textsuperscript{8,9}:

\[ H_{cf}(J) = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_{k}^{q} O_{k}^{q} = \sum_{k=2,4,6} \sum_{q=-k}^{k} a_k (1 - \sigma_k) A_k^q \left\langle r^k \right\rangle O_k^q \tag{S1} \]

where \( k \) is the order (also called rank or degree) and \( q \) is the operator range, that varies between \( k \) and \(-k\), of the Stevens operator equivalents \( O_k^q \) as defined by Ryabov in terms of the angular momentum operators \( J_z \) and \( J_{\nu} \)\textsuperscript{10} where the components \( O_k^q(c) \) and \( O_k^q(s) \) correspond to the ESOs with \( q \geq 0 \) and \( q < 0 \) respectively\textsuperscript{10}. Note that all the Stevens CF parameters \( B_k^q \) are real, whereas the matrix elements of \( O_k^q(q < 0) \) are imaginary. \( a_k \) are the \( \alpha \), \( \beta \) and \( \gamma \) Stevens coefficients\textsuperscript{11} for \( k = 2, 4, 6 \), respectively, which are tabulated and depend on the number of \( f \) electrons. \( \sigma_k \) are the Sternheimer shielding parameters\textsuperscript{12} of the \( 4f \) electronic shell, and \( <r^k> \) are the expectation values of the radius\textsuperscript{12}. 
In SIMPRE, the $A^q_i$ CF parameters are determined by the following relations:

\[
A^0_k = \frac{4\pi}{2k+1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{k0}(\theta_i, \varphi_i) p_{kq}
\] (S2.a)

\[
A^q_k = \frac{4\pi}{2k+1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{kq}^i(\theta_i, \varphi_i) p_{kq}
\] (S2.b)

\[
A^q_k = \frac{4\pi}{2k+1} \sum_{i=1}^{N} \frac{Z_i e^2}{R_i^{k+1}} Z_{kq}^i(\theta_i, \varphi_i) p_{kq}
\] (S2.c)

In the REC model\textsuperscript{13} the ligand is modeled through an effective point charge situated between the lanthanoid and the coordinated atom at a distance $R_i$ from the magnetic center, which is smaller than the real metal-ligand distance ($r_i$). To account for the effect of covalent electron sharing, a radial displacement vector ($D_r$) is defined, in which the polar coordinate $r$ of each coordinated atom is varied, $R_i = r_i - D_r$. The usual procedure is to obtain the $D_r$ parameter of each kind of donor atom from a collective fit of an observable (e.g. energy levels or magnetic properties) for a family of isostructural lanthanide complexes. At the same time, the charge value ($Z_i$) is scanned in order to achieve the minimum deviation between calculated and experimental data, whereas $\theta_i$ and $\varphi_i$ remain constant. We calculate the effective distances of the coordinated atoms using the following formula for $D_r$:

\[
D_r \approx \left( \frac{N_L}{V_M} \right) \cdot \frac{1}{E_M(E_L - E_M)}
\] (S3)

where $N_L$ is the coordination number of the complex ($N_L = 8$), $V_M$ is the valence of the metal ($V_M = 3$), and $E_M$ and $E_L$ are the Pauling electronegativities of the metal ($E_M \approx 1.2$) and the donor atom ($E_L = 3.44$ for oxygen and $3.04$ for nitrogen) respectively.

Such relation is an approximation that was obtained by fitting the experimental energy levels of the ground multiplet of the homoleptic families CsNaYCl\textsubscript{6}:Ln\textsuperscript{3+} and CsNaYF\textsubscript{6}:Ln\textsuperscript{3+}, LiYF\textsubscript{4}:Ln\textsuperscript{3+} and LaCl\textsubscript{3}:Ln\textsuperscript{3+} using the crystal structures and the REC model\textsuperscript{13}. The obtained values of $Dr$ (N) and $Dr$ (O) for the Dy compounds are thus 1.20 Å and 0.98 Å. This strategy allows us to restrict the number of free parameters to 2, i.e. the effective charges of the nitrogen and oxygen atoms, $Z_i$ (N) = 0.160 and $Z_i$ (O) = 0.235, which have been obtained by a two-parameter fit of the $\chi T$ product of NaTbCl\textsubscript{q} and NaDyCl\textsubscript{q} measured under a magnetic field of 0.1 and 1T. In the fitting procedures, we define the relative error $E$ as:
where $\chi_{\text{exp}}$ and $\chi_{\text{theo}}$ are experimental and theoretical magnetic susceptibility, respectively, and $n$ is the number of points.

Subsequently, such REC parameters for both different donor atoms are validated with the correct prediction of the $\chi T$ product of NEtDyClq and KNEtDyClq, with an excellent agreement with the experimental results (Fig. SI5(b) and SI5(c)). According to this description, the first excited state is found at 126 cm$^{-1}$ ($g_z = 19.5$), 49 cm$^{-1}$ ($g_z = 18.5$), 193 cm$^{-1}$ ($g_z = 19.4$) and 154 cm$^{-1}$ ($g_z = 19.2$), for NaDyClq, NEtDyClq and KNEtDyClq respectively, with a wave function with a major contribution of $M_j = \pm 15/2$ (Fig. SI6(b)) in all cases.

$$E = \frac{1}{n} \sum_{i=1}^{n} \left[ \frac{\chi_{\text{theo},i} - \chi_{\text{exp},i}}{\chi_{\text{exp},i}} \right]^2$$

(S4)

**Fig. SI5:** $\chi T$ product of a) NaTbClq (2), b) NEtDyClq (4) and c) KNEtDyClq (5) (experimental data in circles) and theoretical fit/prediction from 2 to 300 K at $H = 1$ T as a solid line.
The calculated wave functions of the ground doublets, dominated by high-$M_J$ contributions ($M_J$(Tb) = ±6 or $M_J$(Dy) = ±15/2) are then compatible with the observed SMM behavior for the four compounds (see Fig. SI6). The different countercations present in each crystallographic structure distort the coordination environment to an extent that is comparable to the differences between two conformers within the same crystal structure. For example, the crystal field effect is slightly larger for (3) derivative (about 873 cm$^{-1}$), compared with (4) (800 cm$^{-1}$) or with the two conformers of (5) (841 and 788 for Dy1 and Dy2 respectively). There is no correlation with the averaged distances between the lanthanide and the donor atoms (2.435 Å (3), 2.443 Å (4), 2.430 Å (5) and 2.436 Å (5')), and thus such differences in the crystal field strength are attributed to the small distortions of the chemical structures due to the crystal packing. In contrast with typically negligible distortions caused by temperature$^{14}$ the differences in the crystallographic sites, induced partially by these countercations, lead to different energy level schemes, as can be seen in fig. SI6(b). As these variations cannot be easily controlled, there is no immediate connection between countercation and dynamic magnetic properties. In any case, the countercation has no effect on our parameterization of the effective charges, as demonstrated by the good agreement between the predictions of the magnetic data of (4) and (5) and the experiment (fig. SI5(b) and SI5(c)).
Figure SI6: Energy level scheme and main $M_J$ contributions to the wave functions of the ground and first excited states of (2) NaTbCl₄ (a) and (3) NaDyCl₄, (4) NEtDyCl₄, and (5) KNEtDyCl₄ (b) predicted by SIMPRE software.
5. AC Measurements

The single ion magnet behavior has been experimentally checked by applying an ac magnetic field at different frequencies. Magnetic compounds didn’t show frequency dependence at zero dc field ($H_{DC}$) but they did when a dc field was applied.

![Figure SI7](image)

**Figure SI7**: Bulk NaDyCl₃ (3) ac measurements at 150 Oe. a) Magnetic susceptibility in phase for different frequencies. b) Magnetic susceptibility out of phase. c) Cole-Cole plots at different temperatures with the corresponding $\alpha$ values. The lines in the Cole-Cole plots are fittings to equation SI7. d) Arrhenius fit with an effective energy barrier $U_{eff} = 63$ cm⁻¹, and a pre-exponential factor $\tau_0 = 1.8 \times 10^{-6}$ s. e) Fit to a Raman relaxation mechanism with $B_{Raman} = 1.0 \times 10^{-9}$ Hz/K².
Figure SI8: Bulk NaDyCl₃ ac measurements at 425 Oe. a) Magnetic susceptibility in phase for different frequencies. b) Magnetic susceptibility out of phase. c) Cole-Cole plot at different temperatures with the corresponding $\alpha$ values. The lines in the Cole-Cole plots are fittings to equation SI7. d) Arrhenius fit with an effective energy barrier $U_{\text{eff}} = 65 \text{ cm}^{-1}$, and a pre-exponential factor $\tau_0 = 2.7 \times 10^{-6} \text{ s}$. e) Fit to a Raman relaxation mechanism with $B_{\text{Raman}} = 1.2 \times 10^{-9} \text{ Hz/K}^{-9}$. 
Figure S19: Bulk NaDyCl₃ (3) ac measurements at 750 Oe. a) Magnetic susceptibility in phase for different frequencies. b) Magnetic susceptibility out of phase. c) Cole-Cole plots at different temperatures with the corresponding α values. The lines in the Cole-Cole plots are fittings to equation SI7. d) Arrhenius fit with an effective energy barrier $U_{\text{eff}} = 75 \text{ cm}^{-1}$, and a pre-exponential factor $\tau_0 = 1.1 \times 10^{-6} \text{ s}$. e) Fit to a Raman relaxation mechanism with $B_{\text{Raman}} = 1.5 \times 10^{-9} \text{ Hz K}^{-9}$.
Figure SI10: Bulk NaDyCl₃ ac measurements at 1000 Oe. a) Magnetic susceptibility in phase for different frequencies. b) Magnetic susceptibility out of phase. c) Cole-Cole plot at different temperatures with the corresponding α values. The lines in the Cole-Cole plots are fittings to equation SI7. d) Arrhenius fit with an effective energy barrier $U_{\text{eff}} = 76$ cm⁻¹, and a pre-exponential factor $\tau_0 = 1.1 \times 10^{-6}$ s. e) Fit to a Raman relaxation mechanism with $B_{\text{Raman}} = 1.53 \times 10^{-9}$ Hz/K⁹.
Figure SI11: a) Extrapolation of the effective energy barrier ($U_{\text{eff}} = 60.1 \, \text{cm}^{-1}$) at zero dc magnetic field for bulk NaDyCl₆ (3). b) Extrapolation of $C$ at zero dc field with $B_{\text{Raman}} = 9.3 \times 10^{-10} \, \text{Hz/K}^9$ for the same compound.

$$
\tau = \tau_0 e^{-\frac{U_{\text{eff}}}{k_B T}}
$$

**Equation SI5:** Arrhenius equation.

$$
\tau^{-1} = B_{\text{Raman}} T^n
$$

**Equation SI6:** Raman relaxation equation.

$$
\chi''(\chi) = \frac{-\chi_T - \chi_S}{2\tan\left(\frac{(1 - \alpha)\pi}{2}\right)} + \sqrt{\frac{(\chi_T - \chi_S)^2}{2\tan\left(\frac{(1 - \alpha)\pi}{2}\right)}}
$$

**Equation SI7:** Cole-Cole equation where $\alpha$ ($0 < \alpha < 1$) is related to the number of relaxation mechanisms, $\chi_T$ is the isothermal susceptibility and $\chi_S$ is the adiabatic susceptibility.

**Table SI8:** Coefficient of determination, $R^2$, of the fits to the Raman and Orbach terms showing a best fit for the Raman relaxation in all cases for the compound (3).

| H(Oe) | $R^2(\tau^{-1} = CT^{1/9})$ | $R^2(\tau^{-1} = \tau_0^{-1}\exp(-U_{\text{eff}}/kT))$ |
|-------|--------------------------|-----------------------------------------------|
| 150   | 0.997                    | 0.983                                         |
| 425   | 0.996                    | 0.957                                         |
| 500   | 0.995                    | 0.954                                         |
| 750   | 0.997                    | 0.966                                         |
| 1000  | 0.996                    | 0.985                                         |
Figure SI12: a) Comparison of the Raman mechanism values for NaDyClq (3) as bulk and sublimated material measured in a SQUID magnetometer. For the linear fit to equation SI5, only the points at high temperature (13 – 20 K) are taken into account. b) Equivalent Raman mechanism fits.

Figure SI13: Magnetic susceptibilities in phase ($\chi'$, left) and out of phase ($\chi''$, right) at a) $H_{DC} = 500$ Oe and b) $H_{DC} = 2000$ Oe of bulk NaTbClq (2).
Figure SI14: Magnetic susceptibilities in phase ($\chi'$, left) and out of phase ($\chi''$, right) at a) $H_{DC} = 500$ Oe and b) $H_{DC} = 2000$ Oe of bulk NEtDyClq (4).
6. Film Characterization

Figure SI15: AFM topography images of NaDyClq (3) molecular layers grown on NiFe (left) and Co (right) substrates.

Figure SI16: Negative and positive modes MALDI-TOF for films of a) NaYClq (1), b)
NaTbClq (2) and c) NaDyClq (3). A pattern was not found in films of NEtDyClq (4) and KNEtDyClq (5).

**Figure SI17:** a) Temperature-dependent magnetization of NiFe (10nm)/NaTbClq where a 1/T behavior is observed in the FC curve whereas a blocking (cusp) appears in the ZFC curve. b) Temperature-dependent magnetization of NiFe (10 nm). $M_{FM}$ has been subtracted in Figures 5b-d and in some cases scaled to $M_{tot}$ at low temperatures before subtraction, as slight variation in the thickness yield different absolute magnetization values. recalcular que el NiFe no tiene 1/T behaviour en el fc ni cusp en el zfc (blocking).
References

(1) Aly, H. F.; Abdel Kerim, F. M.; Kandil, A. T. I.R. Spectra of Lanthanide 8-Hydroxyquinoline Complexes. J. Inorg. Nucl. Chem. 1971, 33, 4340–4344.

(2) Nervik, W. E.; Magee, R. J.; Freiser, H.; Friedel, R.; Hillard, L. E.; Johnson, W. D. I.R. Spectra of Lanthanide 8-Hydroxyquinoline Complexes. 1971, 33, 4340–4344.

(3) Lunghi, A.; Totti, F.; Sessoli, R.; Sanvito, S. The Role of Anharmonic Phonons in under-Barrier Spin Relaxation of Single Molecule Magnets. Nat. Commun. 2017, 8, 14620.

(4) Escalera-Moreno, L.; Suaud, N.; Gaita-Ariño, A.; Coronado, E. Determining Key Local Vibrations in the Relaxation of Molecular Spin Qubits and Single-Molecule Magnets. J. Phys. Chem. Lett. 2017, 8, 1695–1700.

(5) Chilton, N. F.; Deacon, G. B.; Gazukin, O.; Junk, P. C.; Kersting, B.; Langley, S. K.; Moubarak, B.; Murray, K. S.; Schleife, F.; Shome, M.; et al. Structure, Magnetic Behavior, and Anisotropy of Homoleptic Trinuclear Lanthanoid 8-Quinolinolate Complexes. Inorg. Chem. 2014, 53, 2528–2534.

(6) Baldoví, J. J.; Duan, Y.; Morales, R.; Gaita-Ariño, A.; Ruiz, E.; Coronado, E. Rational Design of Lanthanoid Single-Ion Magnets: Predictive Power of the Theoretical Models. Chem. - A Eur. J. 2016, 22, 13532–13539.

(7) Baldoví, J. J.; Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A.; Palii, A. SIMPRE: A Software Package to Calculate Crystal Field Parameters, Energy Levels, and Magnetic Properties on Mononuclear Lanthanoid Complexes Based on Charge Distributions. J. Comput. Chem. 2013, 34, 1961–1967.

(8) Rudowicz, C.; Chung, C. Y. The Generalization of the Extended Stevens Operators to Higher Ranks and Spins, and a Systematic Review of the Tables of the Tensor Operators and Their Matrix Elements. J. Phys. Condens. Matter 2004, 16, 5825–5847.

(9) Rudowicz, C. Transformation Relations for the Conventional Ok Q and Normalised O’k Q Stevens Operator Equivalents with k=1 to 6 and -K≤q≤k. J. Phys. C Solid State Phys 1985, 18, 1415–1430.

(10) Ryabov, I. D. On the Generation of Operator Equivalents and the Calculation of Their Matrix Elements. J. Magn. Reson. 1999, 140, 141–145.

(11) Stevens, K. W. H. Matrix Elements and Operator Equivalents Connected with the Magnetic Properties of Rare Earth Ions. Proc. Phys. Soc. Sect. A 2002, 65, 209–215.

(12) Edvardsson, S.; Klintenberg, M. Role of the Electrostatic Model in Calculating Rare-Earth Crystal-Field Parameters. J. Alloys Compd. 1998, 275–277, 230–233.

(13) Baldoví, J. J.; Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A. Modeling the Properties of Lanthanoid Single-Ion Magnets Using an Effective Point-Charge Approach. Dalton Trans. 2012, 41, 13705.

(14) Qian, K.; Baldoví, J. J.; Jiang, S.-D.; Gaita-Ariño, A.; Zhang, Y.-Q.; Overgaard, J.; Wang, B.-W.; Coronado, E.; Gao, S. Does the Thermal Evolution of Molecular Structures Critically Affect the Magnetic Anisotropy? Chem. Sci. 2015, 6, 4587–4593.
