

## Supplementary information

### Synthesis

Reagents and solvents were purchased from commercial sources. Acetonitrile and hexane were distilled over CaH<sub>2</sub>, and toluene over Na. All procedures for (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (Ga<sub>7</sub>Zn) and for single crystals of (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (Cr<sub>7</sub>Zn) doped in (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (Cr<sub>7</sub>Zn@Ga<sub>7</sub>Zn), were performed under a nitrogen atmosphere.

**(Me<sub>2</sub>NH<sub>2</sub>)[Cr<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>]:** Pivalic acid (35.0 g, 343 mmol), dimethylammonium dimethylcarbamate (1.8 g, 13.4 mmol; as a source of Me<sub>2</sub>NH<sub>2</sub><sup>+</sup>), chromium(III) fluoride tetrahydrate (5.0 g, 27.6 mmol) and basic zinc carbonate (0.6 g, 1.1 mmol), were stirred for 36 h at 160 °C in an Erlenmeyer Teflon® FEP flask. The flask was cooled to room temperature, acetone (80 ml) added to complete precipitation, and the mixture stirred for 1 h. The product was collected by filtration, washed copiously with acetone and then dissolved in pentane (150 ml). The resultant solution was filtered and the solvent from the filtrate removed under reduced pressure. This gave dark green crystalline product. Yield: 8.0 g (90.5 % based on Cr). Elemental analysis calcd (%) for C<sub>82</sub>H<sub>152</sub>Cr<sub>7</sub>F<sub>8</sub>NO<sub>32</sub>Zn: Cr 16.20, Zn 2.91, C 43.86, H 6.82, N 0.62; found: Cr 16.34, Zn 2.89, C 43.50, H 6.99, N 0.52. X-ray quality crystals were obtained by slow evaporation of pentane or toluene solutions of (Me<sub>2</sub>NH<sub>2</sub>)[Cr<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>].

**(Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>]:** A mixture of gallium fluoride trihydrate (3.0 g, 16.6 moles), pivalic acid (24.0 g, 235 mmol), dimethylammonium dimethylcarbamate (0.9 g, 6.7 mmol), basic zinc carbonate (0.6 g, 1.1 mmol) and toluene (25 ml) were heated with stirring at 160 °C for 20 h in a two-neck flask fitted with a distillation condenser to the middle neck and the second connected to a slow flow of nitrogen allowing the gaseous products from the reaction and toluene to leave the flask. The flask was cooled to 50 °C, hexane (100 ml) was added and the solution stirred for 30 min then filtered. Hexane was removed from the filtrate by distillation, and the residue reheated back to 160 °C for 30 min. On cooling to 70 °C, acetonitrile (75 ml) was added and the mixture was vigorously stirred for 15 min, before cooling to room temperature. After 1 h the microcrystalline product was filtered off, washed with acetonitrile and dried in a flow of N<sub>2</sub> at room temperature. The product was dissolved in toluene (50 ml) and filtered prior to evaporating the solvent under a N<sub>2</sub> flow. This gave colourless crystalline (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>](C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>). Yield: 4.5 g (77%, based on Ga). Elemental analysis calcd (%) (C<sub>89</sub>H<sub>160</sub>F<sub>8</sub>Ga<sub>7</sub>NO<sub>32</sub>Zn): Ga, 19.82; Zn, 2.66; C, 43.43; H, 6.55; N, 0.57; found: Ga, 19.55; Zn, 2.61; C 43.06; H 6.92; N, 0.47. X-ray quality crystals of (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (without solvent) were collected directly from the bulk sample before the toluene was evaporated to dryness, and could also be obtained by recrystallisation from ethylacetate or toluene.

**Cr<sub>7</sub>Zn@Ga<sub>7</sub>Zn:** (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (2.5 g) and (Me<sub>2</sub>NH<sub>2</sub>)[Ga<sub>7</sub>ZnF<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (0.0075 g) were dissolved in anhydrous toluene (17 ml) while stirring at 100 °C for 10 min under a N<sub>2</sub> atmosphere. The clear solution was cooled to ambient temperature and left undisturbed. Well shaped X-ray quality crystals, were collected after three days.

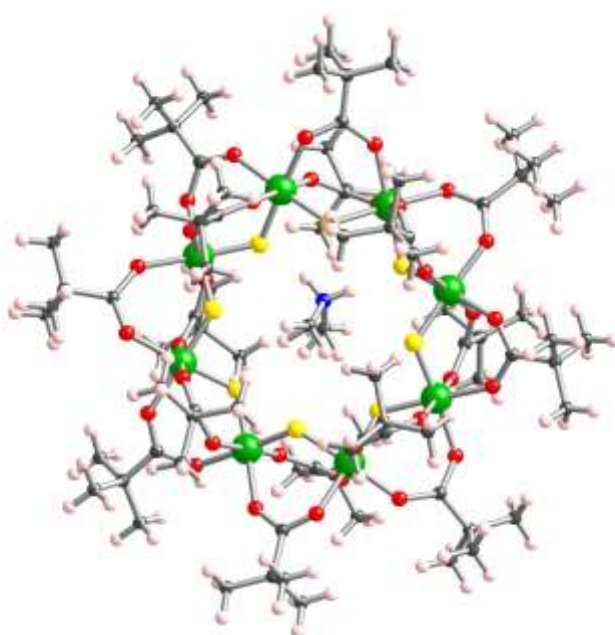
### X-ray diffraction

**Cr<sub>7</sub>Zn:** tetragonal,  $a = b = 19.8766(5)$ ,  $c = 16.0127(12)$  Å,  $U = 6326.3(5)$  Å<sup>3</sup>,  $T = 150$  K, space group  $I4$ ,  $Z = 2$ , 9104 reflections measured, 4355 unique, ( $R_{\text{int}} = 0.0783$ ). Final  $R_1 = 0.1434$ , GOF = 1.051,  $wR_2 [I > 2\sigma(I)] = 0.3702$ .

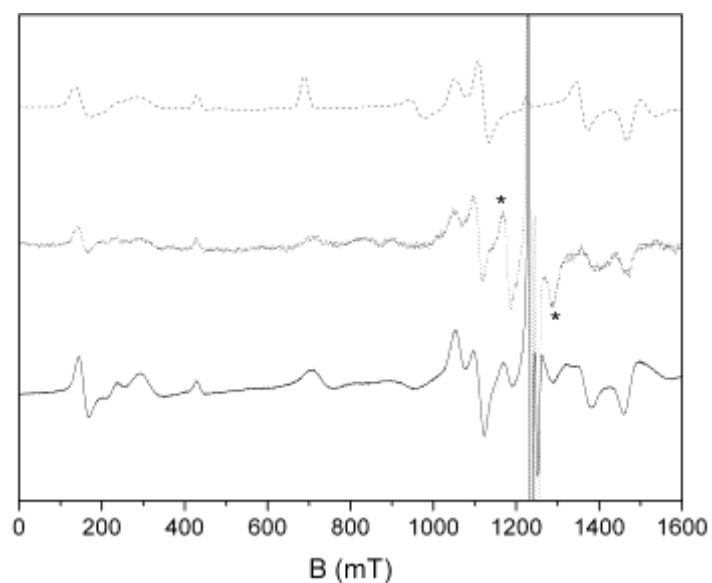
**Cr<sub>7</sub>Zn@Ga<sub>7</sub>Zn**: tetragonal,  $a = b = 19.8454(5)$ ,  $c = 15.8931(6)$  Å,  $U = 6259.3(3)$  Å<sup>3</sup>,  $T = 100$  K, space group  $I4$ ,  $Z = 2$ , 14378 reflections measured, 5191 unique, ( $R_{\text{int}} = 0.0703$ ). Final  $R_1 = 0.0995$ , GOF = 1.155,  $wR_2 [I > 2\sigma(I)] = 0.2611$ .

### Measurements

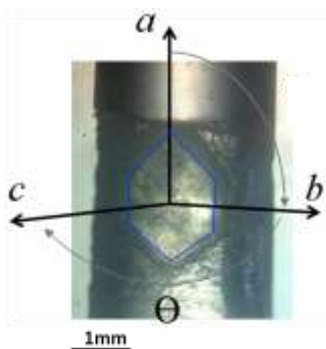
CW and pulsed EPR spectra were recorded on Bruker EMX and Elexsys E580 spectrometers, respectively. EPR simulations used Weihe's SimEPR program, see reference 15 in main text.



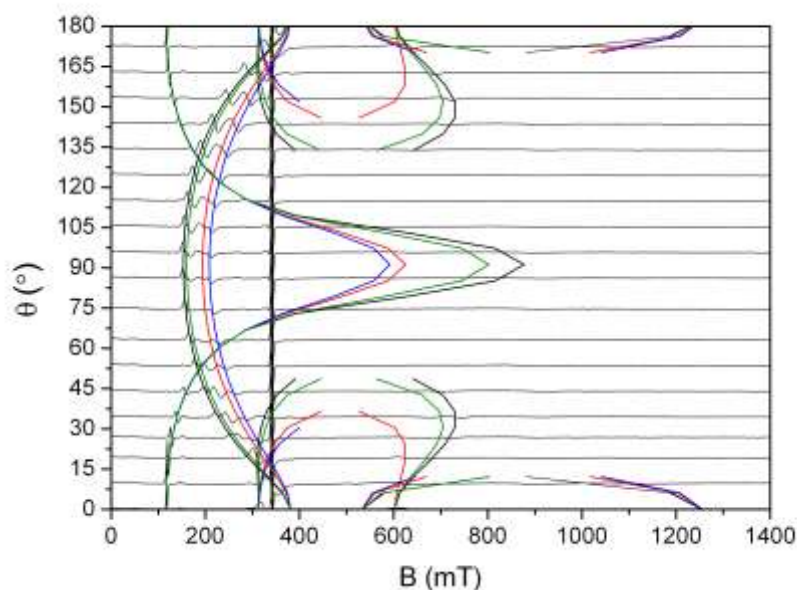
**Figure S1.** Molecular structure of  $(\text{Me}_2\text{NH}_2)[\text{Cr}_7\text{ZnF}_8(\text{O}_2\text{C}^t\text{Bu})_{16}]$  “Cr<sub>7</sub>Zn”. Colour scheme: Cr/Zn (green), O (red), F (yellow), C (black), N (blue), H (white).



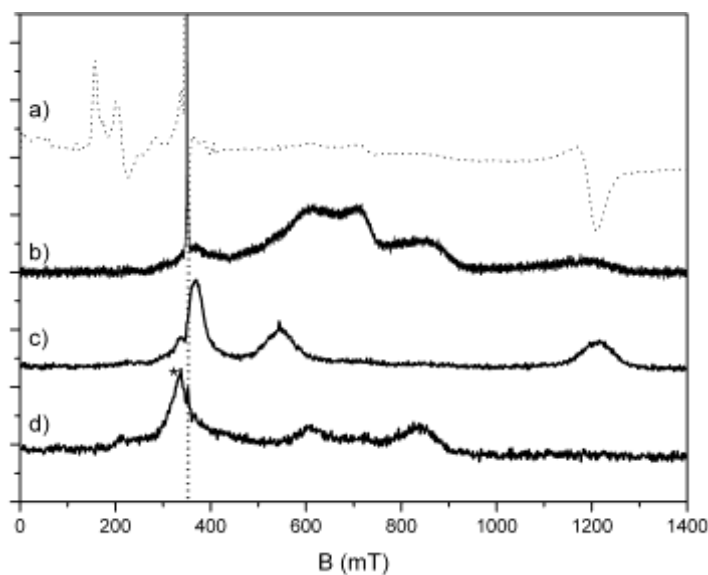
**Figure S2.** CW Q-band EPR spectra of polycrystalline  $\text{Cr}_7\text{Zn}$  (solid line) and  $\text{Cr}_7\text{Zn}@Ga_7\text{Zn}$  (dotted) at 5 K, with simulation (dot-dash) of the  $S = 3/2$  ground state spectrum. The sharp feature at  $g = 1.96$  (1230 mT) and those marked \* arise from the  $S = 1/2$  and  $5/2$  first and second excited states, respectively. This former has significant amplitude only because the spectral intensity is compressed into a very narrow field range.



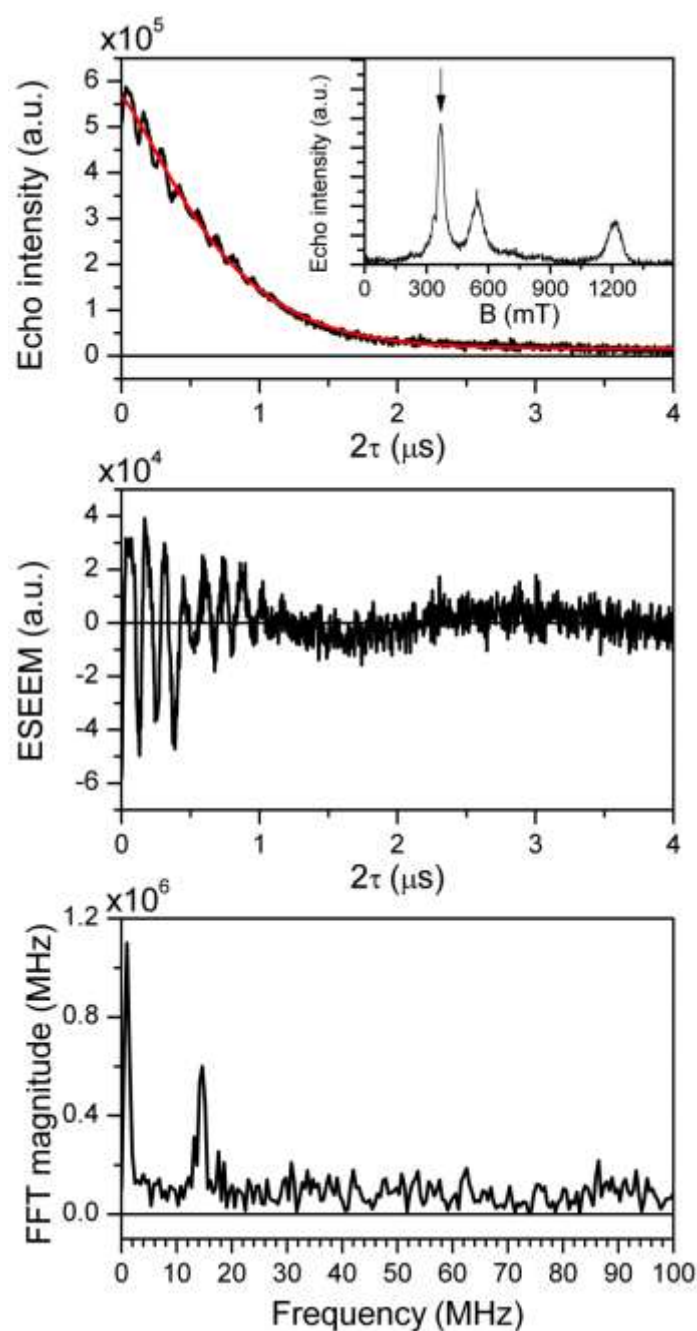
**Figure S3.** Photograph of single crystal of  $\text{Cr}_7\text{Zn}@Ga_7\text{Zn}$  mounted on a vertical face of the quartz sample holder. The boundaries of the (0 -1 -1) face of the colourless crystal are highlighted for clarity. The crystal habit is an elongated hexagonal prism with the crystal  $a$  axis parallel to the elongated direction in the hexagonal (0 -1 -1) face. The crystal  $c$  axis is oriented  $51^\circ$  away from the normal to this face. The direction of the crystal  $abc$  axes, and the experimental rotation angle ( $\theta$ ) about the  $a$  axis, are indicated. The applied field is perpendicular hence allowing EPR measurement in the  $bc$  plane.



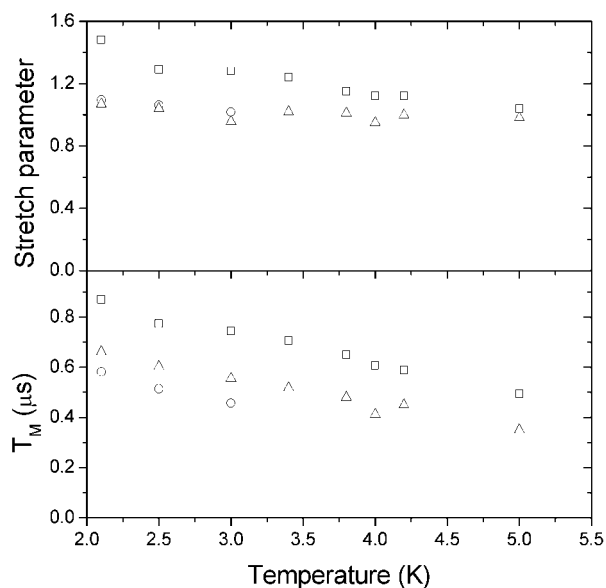
**Figure S4.** CW X-band EPR spectra of a single crystal of  $\text{Cr}_7\text{Zn}@Ga_7\text{Zn}$ , measured in the crystal  $bc$  plane at 5 K. The lines are calculated resonance fields for the molecular azimuthal angles  $\varphi = 16$  (black),  $\varphi+45$  (red),  $\varphi+90$  (blue) and  $\varphi+135^\circ$  (green); see main text for definition of  $\varphi$ .



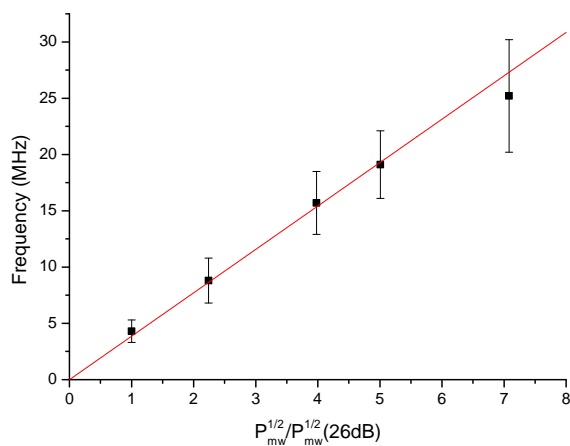
**Figure S5.** (a) CW X-band EPR and (b) field-swept echo-detected (FSED) EPR spectra for a polycrystalline sample of  $\text{Cr}_7\text{Zn}@Ga_7\text{Zn}$  at 5 K. (c) and (d) normalised X-band FSED spectra of a  $\text{Cr}_7\text{Zn}@Ga_7\text{Zn}$  single crystal with  $c||\mathbf{B}$  and  $b||\mathbf{B}$ , respectively, at 5K. The symbol \* indicates an impurity from the resonator. Experimental parameters for CW: 9.678514 GHz, 0.15 mW microwave power (30 dB attenuation), 1 G modulation amplitude and 100 kHz modulation frequency. Experimental parameters for FSED: 16 ns  $\pi/2$  pulse,  $\tau=180$  ns, 999.6  $\mu\text{s}$  shot repetition time, 33 dB video gain, 20 MHz video bandwidth, 8 dB attenuation, 10 shots per loop, 10 averaged scans, 1024 field points.



**Figure S6.** (a) Representative echo decay measurement, for the crystal orientation  $c \parallel \mathbf{B}$  at  $B_0 = 366$  mT and 3 K. Inset: FSED spectrum showing the peak at 3500 G [16 ns  $\pi/2$  pulses,  $\tau = 190$  ns, 1999.2  $\mu\text{s}$  shot repetition time, 57 dB video gain, 20 MHz video bandwidth, 8 dB attenuation, 10 averaged scans, 50 shots per loop, 1024 field points]. Red curve is best fit to the stretched exponential function  $f(2\tau) = f(0)\exp[-(2\tau/T_M)^x]$  giving  $T_M = 745 \pm 3$  ns and  $x = 1.28 \pm 0.01$ . (b) Difference between the echo decay and the fit function reported in (a), revealing ESEEM effect. (c) Fourier transform of (b); the peak at ca. 14 MHz is close to the proton Larmor frequency. The peak at low frequency is an artefact of noise and the non-perfect background correction: the width of the peak cf. its central value indicates that it is not a genuinely oscillatory component of the data.



**Figure S7.** Temperature dependence of  $T_M$  and stretch parameters for the crystal orientation  $c||\mathbf{B}$ , measured at the FSED-EPR peaks at “ $g$ ” = 1.89 (366 mT, squares), 1.27 (545 mT, triangles) and 0.567 (1220 mT, circles). Data measured with a two-step phase cycle sequence. The uncertainties on the  $T_M$  values, as derived from the fits to the echo decay curves (Fig. S6), are within 0.01  $\mu\text{s}$ .



**Figure S8.** Nutation frequency as a function of the square root of applied microwave power relative to that when a high power attenuation of 26dB is applied (black squares; measured at  $B_0 = 1160$  mT and  $c||\mathbf{B}$  at 4.5 K). Error bars are derived from the full width at half maximum of the corresponding peaks in the Fourier transformed data (Fig. 4, main text). The linear least squares fit (red line) was constrained to go through the origin.