Supporting Information

Magnetocaloric Effect in the Quasi-1D Chain Carbonate $NaDy(CO_3)F_2$ Through Crystallographic Directional Rotation

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EXPERIMENTAL SECTION

Reagents. Na_2CO_3 (99.5%, Rhawn), NaF (98%, Macklin), and $Dy(NO_3)_3{\cdot}6H_2O$ (99.9%, Macklin), were used as received.

Synthesis. Tiny single crystals of $NaDy(CO_3)F_2$ were grown using the hydrothermal method. 0.53 g Na_2CO_3 (0.005 mol) and 0.21 g NaF (0.005 mol) were mixed with about 1.14 g (0.0025 mol) of $Dy(NO_3)_3{\cdot}6H_2O$, added to 10 ml H_2O in an autoclave equipped with a PTFE liner (25 mL) to synthesize the samples. The mixture was heated at 220°C for two days, then cooled to room temperature for two days. The rod-shaped crystals were obtained, and the products were washed with deionized water and alcohol alternatively. Single crystals of $NaDy(CO_3)F_2$ were obtained, and both of them were isostructural with $NaYb(CO_3)F_2$[1]. A high-temperature hydrothermal synthesis technique was applied to obtain millimeter-scale crystals to study the anisotropic magnetic properties of $NaDy(CO_3)F_2$. The 0.212 g Na_2CO_3, 0.336 g NaF, 0.457 g $Dy(NO_3)_3{\cdot}6H_2O$, and 2 ml H_2O were mixed into a 10 mm gold linear diameter and placed in a diameter of 22 mm and a volume of 70 ml autoclave. Then the autoclave was placed in the resistance furnace, and the furnace body temperature was set to 500-650 °C; after two days of constant temperature growth, the cooling program was set up, the temperature was slowly reduced to 100 °C, and then it is naturally cooled to room temperature, the autoclave is opened, and the millimeter-level $NaDy(CO_3)F_2$ single crystals were obtained.

Structure Determination and Power X-ray Diffraction (P-XRD). Single crystal X-ray diffraction (SC-XRD) data for $NaDy(CO_3)F_2$ were collected on a Bruker D8 VENTURE diffractometer at 100 K. The detector is PHOTON III C14 with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The raw data were corrected for background, polarization, and Lorentz factor using APEX4 software, and absorption correction based on the multiscan using the SADABS program package. The structures of $NaDy(CO_3)F_2$ were solved through the ShelXT program and refined by the ShelXL least-squares refinement package[2]. Also, the ADDSYM algorithm in the program PLATON was used to trace the possible higher symmetry[3]. The Powder X-ray diffraction (P-XRD) of Na*RE*$(CO_3)F_2$ (*RE* = Tb−Er) was measured on a Rigaku SmartLab 9 KW instrument equipped with CuK-beta radiation, transmission geometry, and a linear BB detector. To ensure the phase purity of the synthesized $NaDy(CO_3)F_2$, P-XRD analysis was performed using the GSAS II software. This refinement indicates a good agreement between the observed and calculated diffraction patterns, confirming the phase purity and structural accuracy of the $NaDy(CO_3)F_2$. The Cambridge Crystallographic Data Centre (CCDC) of $NaDy(CO_3)F_2$ is 2381122.

Infrared (IR) spectroscopy. The Fourier transform infrared spectroscopy (FTIR) spectrum for $NaDy(CO_3)F_2$ was collected on the Excalibur 3100 infrared spectrometer in the range of 600-1600 cm^{-1}.

Physical properties. Magnetic susceptibility was measured using a Quantum Design Magnetic Properties Measurement System (MPMS3) magnetometer. The powder samples of $NaDy(CO_3)F_2$ (9.22 mg) were prepared for magnetization characterization. The temperature dependency of magnetic susceptibility (χ) was measured at B = 0.2 T in the range of 1.8-300 K. The polycrystalline samples were encapsulated within gel capsules affixed to brass rods. Magnetization (M) versus magnetic field (B) curves were performed at 1.8 K from -7 T to 7 T. For the single crystals, GE varnish was used to affix it to a quartz rod. The anisotropic $\chi(T)$ curves from 1.8 to 300 K at 0.2 T and isothermal $M(B)$ from 2 K to 16 K curves of $NaDy(CO_3)F_2$ were measured. The $NaDy(CO_3)F_2$ powder sample was pressed into a pellet with a mass of 1.4 mg for a specific heat test. The Quantum Design Physical Property Measurement System (PPMS) was used to measure the specific heat.

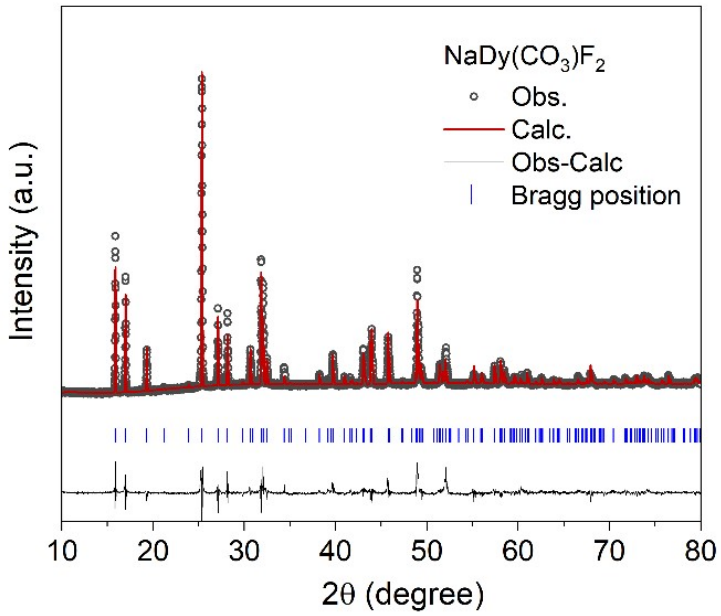

Figure S1. Rietveld plots of P-XRD data for $NaDy(CO_3)F_2$.

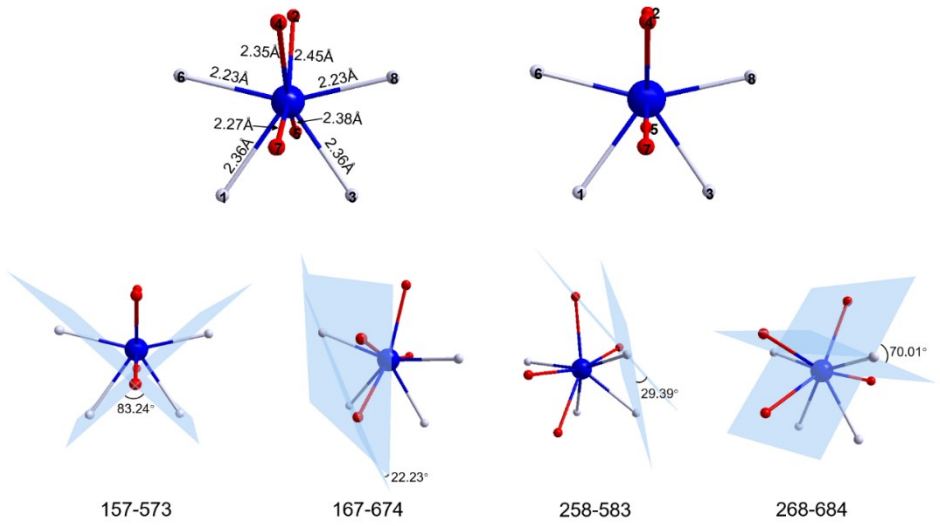

Figure S2. Relevant dihedral angles for the DyO_4F_4 polyhedra in the crystal structure of $NaDy(CO_3)F_2$.

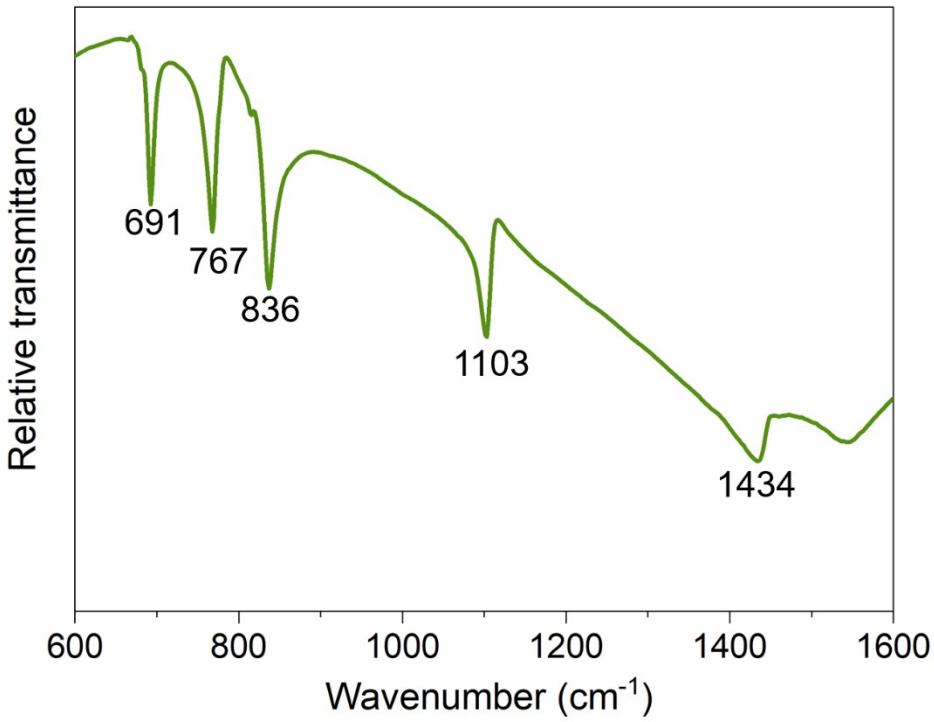

Figure S3. The IR spectroscopy of $NaDy(CO_3)F_2$.

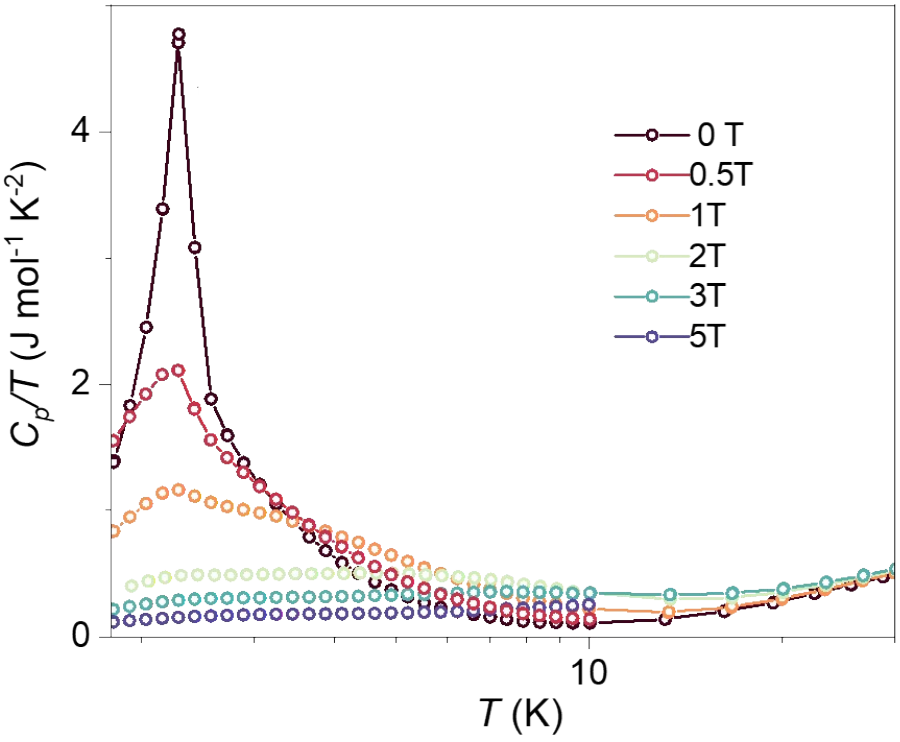

Figure S4. Specific heat divided by temperature, C_p/T, vs T of $NaDy(CO_3)F_2$ polycrystalline sample at several magnetic fields.

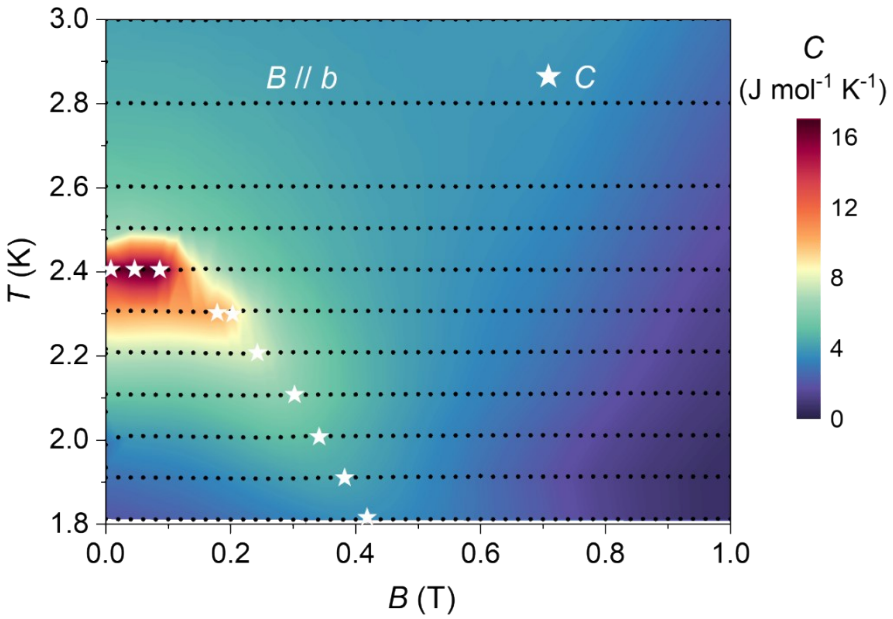

Figure S5. The magnetic phase diagram of $NaDy(CO_3)F_2$ along the crystallographic *b*-axis with $C(T, B)$ measurements data.

Table S1. Crystal Data and Structure Refinements for $NaDy(CO_3)F_2$.

Empirical formula	$NaDy(CO_3)F_2$
Temperature/K	100 K
Crystal system	Orthorhombic
Space group	*Pnma*
Formula weight	283.50
a/Å	6.3264(5)
b/Å	6.9952(6)
c/Å	9.1656(6)
volume/Å^3	405.62(5)
Z	4
ρ_{calc}/g/cm^3	4.642
μ/mm^{-1}	18.469
F(000)	500
Crystal size/mm^3	0.03 × 0.02 × 0.012
radiation	Mo K\α (λ =0.71073)
2θ range for data collection/º	7.328-60.998
Index ranges	-9≤*h*≤9, -9≤*k*≤9, -11≤*l*≤13
Reflections collected	12350
Independent reflections	662 [R_{int} = 0.0549]
Goodness-of-fit on F^2	1.100
Final *R* indexes [$I \geq 2\sigma(I)$]	R1 = 0.0207, wR2 = 0.0513
Final *R* indexes [all data]	R1 = 0.0220, wR2 = 0.0525

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $NaDy(CO_3)F_2$.

	x	y	z	U_{eq}
Dy1	0.01266 (3)	0.250000	0.57837 (2)	0.00412 (12)
Na1	0.1719 (3)	0.250000	0.2178 (2)	0.0110 (4)
F1	0.0418 (3)	0.5607 (3)	0.6308 (2)	0.0072 (4)
O1	0.3680 (5)	0.250000	0.6855 (4)	0.0087 (7)
O2	0.6582 (6)	0.250000	0.5441 (4)	0.0104 (7)
O3	0.3372 (6)	0.250000	0.4461 (4)	0.0085 (7)
C1	0.4601 (9)	0.250000	0.5583 (6)	0.0062 (9)

Table S3. Atomic displacement parameters (Å^2) for $NaDy(CO_3)F_2$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Dy1	0.00472 (16)	0.00426 (16)	0.00337 (16)	0.000	0.00010 (6)	0.000
Na1	0.0087 (9)	0.0191 (11)	0.0053 (9)	0.000	0.0016 (7)	0.000
F1	0.0106 (9)	0.0062 (9)	0.0049 (10)	−0.0002 (8)	−0.0015 (8)	0.0005 (8)
O1	0.0045 (16)	0.0161 (17)	0.0054 (16)	0.000	0.0018 (12)	0.000
O2	0.0028 (16)	0.0204 (19)	0.0079 (16)	0.000	−0.0002 (13)	0.000
O3	0.0042 (16)	0.0165 (17)	0.0048 (15)	0.000	−0.0021 (12)	0.000
C1	0.009 (2)	0.002 (2)	0.007 (2)	0.000	−0.0022 (18)	0.000

Table S4. Geometric parameters (Å) for $NaDy(CO_3)F_2$.

Dy1—Dy1^{i}	3.7846 (3)	Na1—Na1^{viii}	3.2178 (8)
Dy1—Na1^{ii}	3.467 (2)	Na1—F1^{ix}	2.382 (3)
Dy1—Na1	3.455 (2)	Na1—F1^{x}	2.382 (3)
Dy1—F1^{iii}	2.355 (2)	Na1—F1^{iii}	2.347 (3)
Dy1—F1^{iv}	2.233 (2)	Na1—F1^{v}	2.347 (3)
Dy1—F1^{v}	2.355 (2)	Na1—O2^{ii}	2.402 (5)
Dy1—F1	2.233 (2)	Na1—O3^{ii}	2.596 (4)
Dy1—O1	2.453 (3)	Na1—O3	2.339 (4)
Dy1—O1^{vi}	2.350 (3)	Na1—C1^{ii}	2.863 (6)
Dy1—O2^{vii}	2.264 (4)	O1—C1	1.303 (6)
Dy1—O3	2.384 (4)	O2—C1	1.260 (6)
Dy1—C1	2.837 (6)	O3—C1	1.289 (6)
Na1—Na1^{ii}	3.2178 (8)		
Na1^{ii}—Dy1—Dy1^{i}	71.121 (10)	F1^{v}—Na1—Na1^{ii}	47.57 (7)
Na1—Dy1—Dy1^{i}	69.464 (9)	F1^{x}—Na1—Na1^{ii}	144.02 (7)
Na1—Dy1—Na1^{ii}	55.407 (13)	F1^{iii}—Na1—Na1^{viii}	117.24 (10)
F1^{iv}—Dy1—Dy1^{i}	35.49 (5)	F1^{iii}—Na1—Na1^{ii}	47.57 (7)

F1—Dy1—Dy1^{i}	169.89 (6)	F1^{ix}—Na1—Na1^{viii}	46.66 (6)
F1^{iii}—Dy1—Dy1^{i}	33.40 (5)	F1^{ix}—Na1—Na1^{ii}	144.02 (7)
F1^{v}—Dy1—Dy1^{i}	101.80 (5)	F1^{x}—Na1—Na1^{viii}	46.66 (6)
F1^{iii}—Dy1—Na1^{ii}	43.25 (6)	F1^{v}—Na1—Na1^{viii}	117.24 (10)
F1^{iv}—Dy1—Na1^{ii}	102.70 (5)	F1^{v}—Na1—F1^{ix}	108.81 (9)
F1^{iv}—Dy1—Na1	100.47 (6)	F1^{iii}—Na1—F1^{ix}	161.81 (12)
F1^{v}—Dy1—Na1^{ii}	43.25 (6)	F1^{ix}—Na1—F1^{x}	67.57 (12)
F1—Dy1—Na1	100.47 (6)	F1^{iii}—Na1—F1^{v}	68.71 (12)
F1^{iii}—Dy1—Na1	42.61 (6)	F1^{v}—Na1—F1^{x}	161.81 (12)
F1—Dy1—Na1^{ii}	102.69 (5)	F1^{iii}—Na1—F1^{x}	108.81 (9)
F1^{v}—Dy1—Na1	42.61 (6)	F1^{v}—Na1—O2^{ii}	124.77 (11)
F1^{iv}—Dy1—F1	153.36 (11)	F1^{iii}—Na1—O2^{ii}	124.77 (11)
F1—Dy1—F1^{iii}	137.25 (6)	F1^{x}—Na1—O2^{ii}	72.10 (10)
F1^{iv}—Dy1—F1^{iii}	68.90 (9)	F1^{ix}—Na1—O2^{ii}	72.10 (10)
F1^{iv}—Dy1—F1^{v}	137.25 (6)	F1^{iii}—Na1—O3^{ii}	82.67 (10)
F1^{iii}—Dy1—F1^{v}	68.43 (11)	F1^{ix}—Na1—O3^{ii}	115.25 (10)
F1—Dy1—F1^{v}	68.90 (9)	F1^{v}—Na1—O3^{ii}	82.67 (10)
F1—Dy1—O1	80.69 (6)	F1^{x}—Na1—O3^{ii}	115.25 (10)
F1^{v}—Dy1—O1	117.37 (8)	F1^{v}—Na1—C1^{ii}	104.67 (12)
F1^{iii}—Dy1—O1	117.37 (8)	F1^{x}—Na1—C1^{ii}	93.43 (12)
F1^{iv}—Dy1—O1^{vi}	80.45 (6)	F1^{ix}—Na1—C1^{ii}	93.43 (12)
F1^{iv}—Dy1—O1	80.69 (6)	F1^{iii}—Na1—C1^{ii}	104.67 (12)
F1—Dy1—O1^{vi}	80.45 (6)	O2^{ii}—Na1—Dy1^{viii}	40.52 (9)
F1^{iv}—Dy1—O2^{vii}	96.41 (6)	O2^{ii}—Na1—Dy1	160.99 (12)
F1—Dy1—O2^{vii}	96.41 (6)	O2^{ii}—Na1—Na1^{viii}	102.63 (12)
F1^{v}—Dy1—O3	73.27 (8)	O2^{ii}—Na1—Na1^{ii}	98.51 (12)
F1^{iii}—Dy1—O3	73.27 (8)	O2^{ii}—Na1—O3^{ii}	52.58 (12)
F1—Dy1—O3	92.19 (6)	O2^{ii}—Na1—C1^{ii}	25.83 (13)
F1^{iv}—Dy1—O3	92.19 (6)	O3^{ii}—Na1—Dy1	108.41 (10)
F1^{iv}—Dy1—C1	86.08 (6)	O3^{ii}—Na1—Dy1^{viii}	93.10 (10)
F1—Dy1—C1	86.08 (6)	O3—Na1—Dy1	43.51 (9)
F1^{v}—Dy1—C1	95.35 (10)	O3—Na1—Dy1^{viii}	114.98 (12)
F1^{iii}—Dy1—C1	95.35 (10)	O3^{ii}—Na1—Na1^{ii}	45.93 (9)
O1^{vi}—Dy1—Dy1^{i}	109.461 (18)	O3—Na1—Na1^{viii}	52.87 (11)
O1—Dy1—Dy1^{i}	100.99 (3)	O3^{ii}—Na1—Na1^{viii}	155.22 (13)
O1^{vi}—Dy1—Na1	174.03 (9)	O3—Na1—Na1^{ii}	105.99 (13)
O1—Dy1—Na1	96.64 (9)	O3—Na1—F1^{v}	74.25 (10)
O1—Dy1—Na1^{ii}	152.05 (9)	O3—Na1—F1^{x}	87.68 (11)
O1^{vi}—Dy1—Na1^{ii}	118.62 (9)	O3—Na1—F1^{ix}	87.68 (11)
O1^{vi}—Dy1—F1^{iii}	133.84 (8)	O3—Na1—F1^{iii}	74.25 (10)
O1^{vi}—Dy1—F1^{v}	133.84 (8)	O3—Na1—O2^{ii}	155.51 (15)
O1^{vi}—Dy1—O1	89.33 (6)	O3—Na1—O3^{ii}	151.91 (15)
O1^{vi}—Dy1—O3	143.48 (12)	O3—Na1—C1^{ii}	178.67 (17)
O1^{vi}—Dy1—C1	116.64 (13)	O3^{ii}—Na1—C1^{ii}	26.75 (13)

O1—Dy1—C1	27.31 (13)	C1^{ii}—Na1—Dy1	135.16 (13)
O2^{vii}—Dy1—Dy1^{i}	84.57 (4)	C1^{ii}—Na1—Dy1^{viii}	66.35 (12)
O2^{vii}—Dy1—Na1^{ii}	43.56 (10)	C1^{ii}—Na1—Na1^{viii}	128.46 (15)
O2^{vii}—Dy1—Na1	98.96 (10)	C1^{ii}—Na1—Na1^{ii}	72.68 (13)
O2^{vii}—Dy1—F1^{iii}	75.05 (9)	Dy1—F1—Dy1^{v}	111.10 (9)
O2^{vii}—Dy1—F1^{v}	75.05 (9)	Dy1—F1—Na1^{v}	128.96 (10)
O2^{vii}—Dy1—O1^{vi}	75.06 (13)	Dy1^{v}—F1—Na1^{xi}	94.08 (9)
O2^{vii}—Dy1—O1	164.39 (13)	Dy1—F1—Na1^{xi}	132.53 (10)
O2^{vii}—Dy1—O3	141.45 (12)	Na1^{v}—F1—Dy1^{v}	94.58 (9)
O2^{vii}—Dy1—C1	168.30 (14)	Na1^{v}—F1—Na1^{xi}	85.77 (7)
O3—Dy1—Dy1^{i}	80.99 (3)	Dy1^{xii}—O1—Dy1	136.51 (15)
O3—Dy1—Na1^{ii}	97.90 (9)	C1—O1—Dy1	93.0 (3)
O3—Dy1—Na1	42.49 (9)	C1—O1—Dy1^{xii}	130.5 (3)
O3—Dy1—O1	54.15 (12)	Dy1^{xiii}—O2—Na1^{viii}	95.92 (14)
O3—Dy1—C1	26.84 (13)	C1—O2—Dy1^{xiii}	166.1 (4)
C1—Dy1—Dy1^{i}	91.01 (4)	C1—O2—Na1^{viii}	98.0 (3)
C1—Dy1—Na1	69.33 (11)	Dy1—O3—Na1^{viii}	175.21 (16)
C1—Dy1—Na1^{ii}	124.74 (11)	Na1—O3—Dy1	94.00 (13)
Dy1—Na1—Dy1^{viii}	158.49 (7)	Na1—O3—Na1^{viii}	81.20 (11)
Na1^{ii}—Na1—Dy1	62.48 (7)	C1—O3—Dy1	96.5 (3)
Na1^{viii}—Na1—Dy1	96.38 (9)	C1—O3—Na1^{viii}	88.2 (3)
Na1^{viii}—Na1—Dy1^{viii}	62.11 (6)	C1—O3—Na1	169.4 (3)
Na1^{ii}—Na1—Dy1^{viii}	139.03 (10)	Dy1—C1—Na1^{viii}	121.61 (19)
Na1^{ii}—Na1—Na1vi^{ii}	158.86 (14)	O1—C1—Dy1	59.7 (3)
F1^{x}—Na1—Dy1	122.83 (8)	O1—C1—Na1^{viii}	178.7 (4)
F1^{v}—Na1—Dy1^{viii}	145.22 (6)	O2—C1—Dy1	177.8 (4)
F1^{iii}—Na1—Dy1	42.81 (6)	O2—C1—Na1^{viii}	56.2 (3)
F1^{x}—Na1—Dy1^{viii}	42.66 (6)	O2—C1—O1	122.5 (5)
F1^{v}—Na1—Dy1	42.81 (6)	O2—C1—O3	121.2 (5)
F1^{iii}—Na1—Dy1^{viii}	145.22 (6)	O3—C1—Dy1	56.6 (3)
F1^{ix}—Na1—Dy1	122.83 (8)	O3—C1—Na1^{viii}	65.0 (3)
F1^{ix}—Na1—Dy1^{viii}	42.66 (6)	O3—C1—O1	116.3 (5)

Symmetry codes: (i) −x, −y, −z+1; (ii) x−1/2, y, −z+1/2; (iii) −x, y−1/2, −z+1; (iv) x, −y+1/2, z; (v) −x, −y+1, −z+1; (vi) x−1/2, y, −z+3/2; (vii) x−1, y, z; (viii) x+1/2, y, −z+1/2; (ix) −x+1/2, −y+1, z−1/2; (x) −x+1/2, y−1/2, z−1/2; (xi) −x+1/2, −y+1, z+1/2; (xii) x+1/2, y, −z+3/2; (xiii) x+1, y, z.

Table S5. Selected bond lengths (Å), bond valence (BV), and bond valence sum (BVS) for Na*Dy*(CO_3)F_2.

Bond	Bond length (Å)	BV (v.u.)
Dy1—F1	2.2335	0.4103
Dy1—F1	2.3554	0.3091
Dy1—F1	2.3554	0.3091
Dy1—F1	2.2335	0.4103
Dy1—O1	2.4531	0.3158
Dy1—O1	2.3498	0.4020
Dy1—O2	2.2644	0.4910
Dy1—O3	2.3844	0.3708
Na1—F1	2.3812	0.1364
Na1—F1	2.3466	0.1466
Na1—F1	2.3812	0.1364
Na1—F1	2.3466	0.146
Na1—O2	2.4020	0.1743
Na1—O3	2.5962	0.1164
Na1—O3	2.3393	0.1986
C1—O1	1.3033	1.2272
C1—O2	1.2600	1.3475
C1—O3	1.2893	1.2650

Atom	Dy	Na	C	O1	O2	O3	F
BVS (v.u.)	3.0966	1.1410	3.9786	2.0173	2.0885	1.9953	1.0575

Table S6. Weiss temperatures (Θ), Curie constant (*C*), temperature-independent contribution (χ_0), and effective moments (μ_{eff}) are determined by fitting the Curie−Weiss law to the magnetic susceptibility data.

$\chi = \chi_0 + C/(T-\Theta)$				
Temperature range (K)	Θ (K)	*C*	χ_0	μ_{eff}
15-30	0.19(3)	15.56	-0.00271	11.16
150-300	-7.66(12)	16.97	-0.00474	11.65

Reference

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