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Icosahedral Na_4@Ln_{12}@L_{20} Nanocages Nested by a {Na_4} Parallelogram core and a {L_{20}} Dodecahedral shell

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Experimental Section

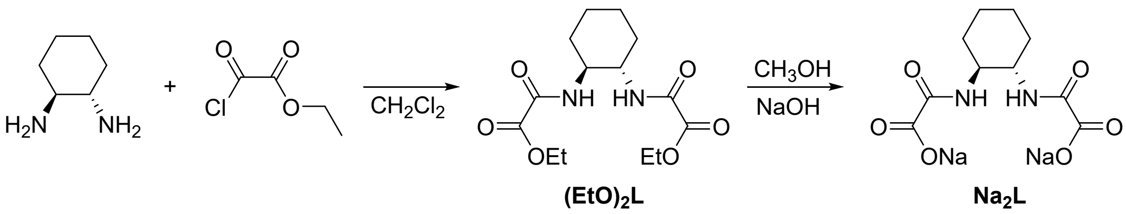
General Materials and Methods

All reagents were of analytical grade and used as received without further purification. ^{1}HNMR spectra were obtained on a BRUKER Ascend 500 (Figs. S13, S14). The ^{1}H NMR (500 MHz) chemical shifts were measured relative to CD_2Cl_2 as the internal reference. IR spectra were measured on a PerkinElmer Spectrum One Fourier transform infrared (FT-IR) spectrometer in the range of 4000-400 cm^{-1} (Figs. S15). Elemental analysis for C, H, and N was conducted using a PerkinElmer model 2400 II elemental analyzer. Powder X-Ray Diffraction (PXRD) pattern was recorded using Cu-*K*α radiation on a PANalytical X'Pert PRO diffractometer (Figs. S16). Thermogravimetric (TG) analysis was performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under a N_2 atmosphere (Figs. S17). Magnetic measurements were performed on polycrystalline samples using a Quantum Design MPMS3 SQUID magnetometer. The variable-temperature magnetic susceptibility data were collected over 300-2.0 K, and the isothermal magnetization measurements were carried out between 0 and 7 T. Dynamic ac susceptibilities were measured under different external direct-current (dc) fields with an ac field of 2 Oe and frequencies ranging from 1 to 1000 Hz.

Synthesis of sodium *N*, *N′*-bis(oxoacetate)-(1*R*, 2*R*)-diaminocyclohexane (Na_2L)

1*R*, 2*R*-cyclohexanediamine (20 mmol) and triethylamine (40 mmol) was dissolved in 50 mL CH_2Cl_2. Ethyl chlorooxoacetate (40 mmol) was then added dropwise while maintaining the reaction solution at a low temperature. The resulting solution was stirred at room temperature for 1 hour, after which 10 mL saturated $NaHCO_3$ aqueous solution was added to quench the reaction. The resultant mixture was extracted with 10 mL of CH_2Cl_2 for three times, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. A brown oily liquid of diethyl *N*, *N′*-bis(oxoacetate)-(1*R*, 2*R*)-diaminocyclohexane [$(EtO)_2L$] was obtained with a yield of 51%. ^{1}H NMR (500 MHz; CD_2Cl_2): δ 7.47 (d, *J* = 8.2 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 4.19 (t, *J* = 8.3 Hz, 2H), 1.81 (d, *J* = 13.3 Hz, 2H), 1.63 (dd, *J* = 13.3, 7.7 Hz, 2H), 1.59-1.51 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 6H). IR (KBr, cm^{-1}): *ν* = 3477 (s), 2836 (m), 2734 (m), 1621 (s), 1357 (s), 1170 (w), 1106 (w), 985 (w), 777 (m), 572 (w).

Subsequently, $(EtO)_2L$ (4.78 mmol) and NaOH (9.56 mmol) was dissolved in 40 mL anhydrous CH_3OH. After refluxing for 1 h, a white precipitate of sodium *N*, *N'*-bis(oxoacetate)-(1*R*, 2*R*)-diaminocyclohexane (Na_2L) was formed. The precipitate was then flited out, washed with CH_3OH, and dried in vacuum. Yield: 46%。 ^1H NMR (500 MHz; CD_2Cl_2): δ 4.15-4.03 (m, 2H), 1.71 (dq, J = 10.8, 6.8, 5.5 Hz, 4H), 1.67-1.57 (m, 2H), 1.51 (t, J = 6.0 Hz, 2H). IR (KBr, cm^{-1}): v = 3477 (s), 2836 (m), 2734 (m), 1621 (s), 1357 (s), 1170 (w), 1106 (w), 985 (w), 777 (m), 572 (w) .



Scheme S1 The synthesis route of **Na_2L**.

Synthesis of $Na_4@Gd_{12}@L_{20}$ and $Na_4@Dy_{12}@L_{20}$

A mixture of Na_2L (0.2 mmol), $Ln(NO_3)_3·6H_2O$ (0.1 mmol) and anthracene-9-carboxylic acid (0.1 mmol) was added into a Teflon liner of vessel. After addition of 2 mL acetonitrile, 2 mL methanol, and 2 mL deionized water, the resultant solution was stirred at room temperature for 30 minutes, followed by the addition of 3 drops of triethylamine. Then the reaction solution was sealed and kept in a 100 °C oven for 72 h. Colorless octahedral crystals were obtained upon cooling to room temperature.

$[Na_4Gd_{12}L_{20}(H_2O)_6]·38H_2O$ (**$Na_4@Gd_{12}@L_{20}$**). Yield: 42% (based on Gd salt). Anal. Calcd. for $C_{348}H_{296}Gd_{10}N_{26}O_{74}$: C, 33.15; H, 3.56; N, 7.73%; expl.: C, 33.24; H, 3.27; N, 7.54. IR (KBr, cm^{-1}): v = 1648 (s), 1548 (m), 1392 (m), 1250 (s), 1141(w), 1092 (w), 941 (m), 898 (w)。

$[Na_4Dy_{12}L_{20}(H_2O)_6]·20H_2O·CH_3CN$ (**$Na_4@Dy_{12}@L_{20}$**). Yield: 47% (based on Dy salt). Anal. Calcd. for $C_{348}H_{296}Dy_{10}N_{26}O_{74}$: C, 33.15; H, 3.56; N, 7.73%; expl.C, 33.24; H, 3.27; N, 7.54. IR (KBr, cm^{-1}): v = 1651 (s), 1549 (m), 1392 (m), 1251 (s), 1141(w), 1092 (w), 941 (m), 898 (w)。

Single-crystal X-ray Crystallography

All data were collected on an Agilent Supernova diffractometer by using graphite-monochromatized

Mo Kα radiation (λ = 0.710 Å). The absorption effect was corrected by semiempirical methods. The absorption effect was corrected with a semiempirical method. The structures were solved by direct methods and refined by full-matrix least-squares method with a suite of SHELX programs *via* the Olex2 interface.[S1-S4] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was performed referring to observed reflections and variable parameters. Some serious disordered solvent molecules in the lattice were treated using the solvent mask of Olex2 software during the structural refinement.

CCDC 2537667 (**$Na_4@Gd_{12}@L_{20}$**) and CCDC 2537668 (**$Na_4@Dy_{12}@L_{20}$**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data and relevant refinement parameters re given in Table S8. Selected structural parameters are given in Tables S9, S10.

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Supplementary Figures and Tables

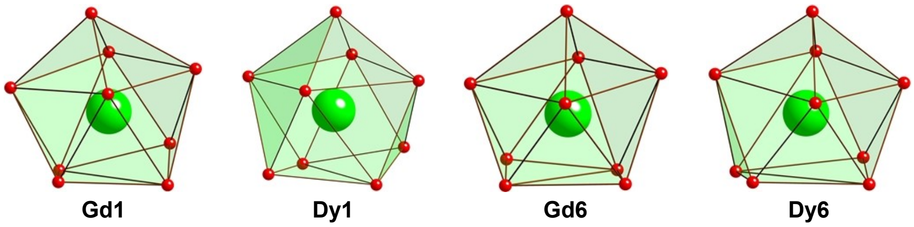


Fig. S1. Coordination geometries of Ln1 and Ln6 ions (Ln = Gd, Dy).

Table S1. Calculated CShM parameters of Ln1 and Ln6 ions (Ln = Gd, Dy).

Configuration	Symmetry	CShM values			
		Gd1	Dy1	Gd6	Dy6
Enneagon	D_{9h}	36.806	36.853	36.751	36.838
Octagonal pyramid	C_{8v}	22.221	22.162	21.618	21.661
Heptagonal bipyramid	D_{7h}	19.163	19.119	19.129	19.177
Johnson triangular cupola J3	O_{3v}	16.050	16.021	15.593	15.520
Capped cube J8	C_{4v}	9.893	9.771	9.358	9.338
Spherical-relaxed capped cube	C_{4v}	8.762	8.680	8.197	8.185
Capped square antiprism J10	C_{4v}	1.532	1.474	1.592	1.577
Spherical capped square antiprism	$\mathbf{C_{4v}}$	**0.628**	**0.610**	**0.717**	**0.707**
Tricapped trigonal prism J51	D_{3h}	2.385	2.403	3.345	3.367
Spherical tricapped trigonal prism	D_{3h}	0.770	0.811	1.491	1.508
Tridiminished icosahedron J63	C_{3v}	12.734	12.698	11.950	11.964
Hula-hoop	C_{2v}	11.560	11.451	11.376	11.373
Muffin	*Cs*	0.929	0.926	1.084	1.047

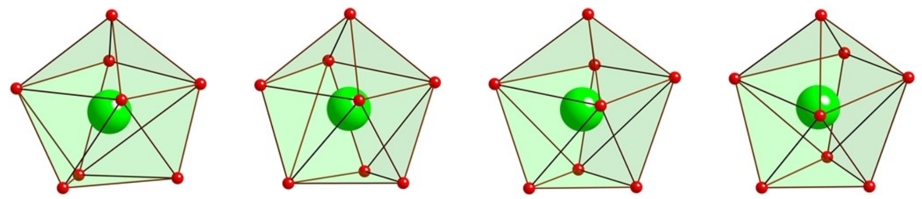


Fig. S2. Coordination geometries of Ln2 and Ln5 ions (Ln = Gd, Dy).

Table S2. Calculated CShM parameters of Ln2 and Ln5 ions (Ln = Gd, Dy).

Configuration	**Symmetry**	**CShM values**			
		Gd2	**Dy2**	**Gd5**	**Dy5**
Octagon	D_{8h}	28.688	28.568	27.822	27.887
Heptagonal pyramid	C_{7v}	23.172	23.328	23.443	23.523
Hexagonal bipyramid	D_{6h}	16.204	16.148	17.002	17.111
Cube	O_h	11.201	11.157	11.597	11.466
Square antiprism	C_{4d}	1.977	1.834	1.494	1.483
Triangular dodecahedron	$\boldsymbol{C_{2d}}$	**1.324**	**1.353**	**1.364**	**1.308**
Johnson gyrobifastigium J26	C_{2d}	13.368	13.546	14.212	14.253
Johnson elongated triangular bipyramid J14	C_{3h}	26.330	26.317	26.425	26.505
Biaugmented trigonal prism J50	D_{2v}	2.229	2.213	1.999	2.157
Biaugmented trigonal prism	D_{2v}	1.720	1.709	3.361	1.944
Snub diphenoid J84	C_{2d}	3.455	3.518	12.421	3.312
Triakis tetrahedron	T_d	12.000	11.957	21.936	12.298
Elongated trigonal bipyramid	D_{3h}	22.029	22.000	22.045	22.045

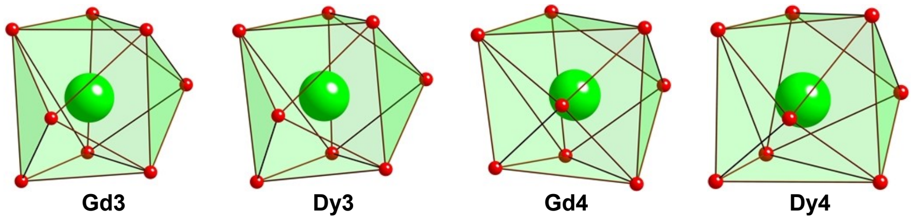


Fig. S3. Coordination geometries of Ln3 and Ln4 ions (Ln = Gd, Dy).

Table S3. Calculated CShM parameters of Ln3 and Ln4 ions (Ln = Gd, Dy).

Configuration	**Symmetry**	**CShM values**			
		Gd3	**Dy3**	**Gd4**	**Dy4**
Octagon	D_{8h}	26.951	27.187	30.640	30.793
Heptagonal pyramid	C_{7v}	20.905	21.499	22.230	22.335
Hexagonal bipyramid	D_{6h}	17.117	16.889	16.460	16.357
Cube	O_h	14.073	13.678	11.893	11.832
Square antiprism	C_{4d}	3.278	2.892	2.485	2.515
Triangular dodecahedron	C_{2d}	2.825	2.571	1.775	1.765
Johnson gyrobifastigium J26	C_{2d}	12.535	12.627	13.503	13.347
Johnson elongated triangular bipyramid J14	C_{3h}	25.712	26.089	25.922	26.377
Biaugmented trigonal prism J50	D_{2v}	1.750	1.575	2.048	1.987
Biaugmented trigonal prism	$\boldsymbol{D_{2v}}$	**1.073**	**0.966**	**1.390**	**1.299**
Snub diphenoid J84	C_{2d}	4.009	3.814	3.908	3.967
Triakis tetrahedron	T_d	14.580	14.189	12.688	12.609
Elongated trigonal bipyramid	D_{3h}	22.550	22.874	21.462	21.903

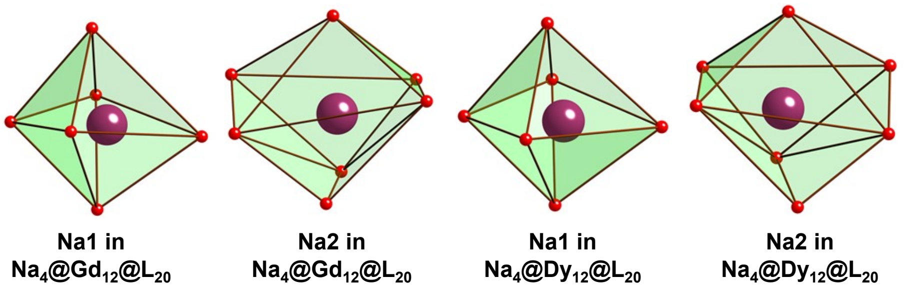


Fig. S4. Coordination geometries of Na ions.

Table S4. Calculated CShM parameters of Na ions.

Configurations	Symmetry	CShM values	
		Na1 in $Na_4@Gd_{12}@L_{20}$	**Na1 in $Na_4@Dy_{12}@L_{20}$**
Hexagon	D_{6h}	32.377	32.507
Pentagonal pyramid	C_{5v}	23.480	23.606
Octahedron	O_h	**3.758**	**3.631**
Trigonal prism	D_{3h}	13.205	13.031
Johnson pentagonal pyramid J2	C_{5v}	25.597	25.719
Configurations	**Symmetry**	**CShM values**	
		Na2 in $Na_4@Gd_{12}@L_{20}$	**Na2 in $Na_4@Dy_{12}@L_{20}$**
Heptagon	D_{7h}	33.502	32.795
Hexagonal pyramid	C_{6v}	14.422	14.285
Pentagonal bipyramid	D_{5h}	12.149	12.337
Capped octahedron	C_{3v}	**5.339**	**5.226**
Capped trigonal prism	C_{2v}	6.480	6.457
Johnson pentagonal bipyramid J13	D_{5h}	15.581	15.856
Johnson elongated triangular pyramid J7	C_{3v}	14.520	14.208

Table S5. The distances between the adjacent Ln^{III} ions in **$Na_4@Gd_{12}@L_{20}$** and **$Na_4@Dy_{12}@L_{20}$**.

Distances	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**
Gd1···Gd2	7.4065(1)	Gd1···Gd6	6.3577(1)	Gd1···Gd3^{i}	6.0821(1)	Gd1···Gd4^{i}	6.4006(1)
Gd2···Gd3	7.1728(1)	Gd2···Gd6	6.2285(1)	Gd2···Gd4^{i}	6.2269(1)	Gd2···Gd5^{i}	6.2238(1)
Gd3···Gd4	7.5207(1)	Gd3···Gd6	7.0593(1)	Gd3···Gd1^{i}	6.0821(1)	Gd3···Gd5^{i}	6.3946(1)
Gd4···Gd5	6.5297(1)	Gd4···Gd6	6.3830(1)	Gd4···Gd1^{i}	6.4006(1)	Gd4···Gd2^{i}	6.2269(1)
Gd5···Gd1	6.4078(1)	Gd5···Gd6	6.2485(1)	Gd5···Gd2^{i}	6.2238(1)	Gd5···Gd3^{i}	6.3946(1)
Distances	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**
Dy1···Dy2	7.3821(0)	Dy1···Dy6	6.3436(0)	Dy1···Dy3^{i}	6.0666(0)	Dy1···Dy4^{i}	6.3962(0)
Dy2···Dy3	7.1467(0)	Dy2···Dy6	6.2129(0)	Dy2···Dy4^{i}	6.1929(1)	Dy2···Dy5^{i}	6.2011(0)
Dy3···Dy4	7.5564(0)	Dy3···Dy6	7.0455(1)	Dy3···Dy1^{i}	6.0666(0)	Dy3···Dy5^{i}	6.3714(0)
Dy4···Dy5	6.4992(0)	Dy4···Dy6	6.3771(0)	Dy4···Dy1^{i}	6.3962(0)	Dy4···Dy2^{i}	6.1929(1)
Dy5···Dy1	3.3788(1)	Dy5···Dy6	6.2429(0)	Dy5···Dy2^{i}	6.2011(0)	Dy5···Dy3^{i}	6.3714(0)

Table S6. The distances between Ln^{III} ion and meaning center of **$Na_4@Gd_{12}@L_{20}$** and **$Na_4@Dy_{12}@L_{20}$**.

Distances	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**
Gd1···Center	6.3211(1)	Gd3···Center	7.1021(1)	Gd5···Center	6.2097(1)
Gd2···Center	6.4605(1)	Gd4···Center	6.2253(1)	Gd6···Center	5.0138(1)
Distances	**Length/Å**	**Distances**	**Length/Å**	**Distances**	**Length/Å**
Dy1···Center	6.2865(0)	Dy3···Center	7.0967(0)	Dy5···Center	6.1947(0)
Dy2···Center	6.4395(0)	Dy4···Center	6.2227(0)	Dy6···Center	5.0052(0)

symmetric code: (i) 1-*x*, 1-*y*, 1-*z*.

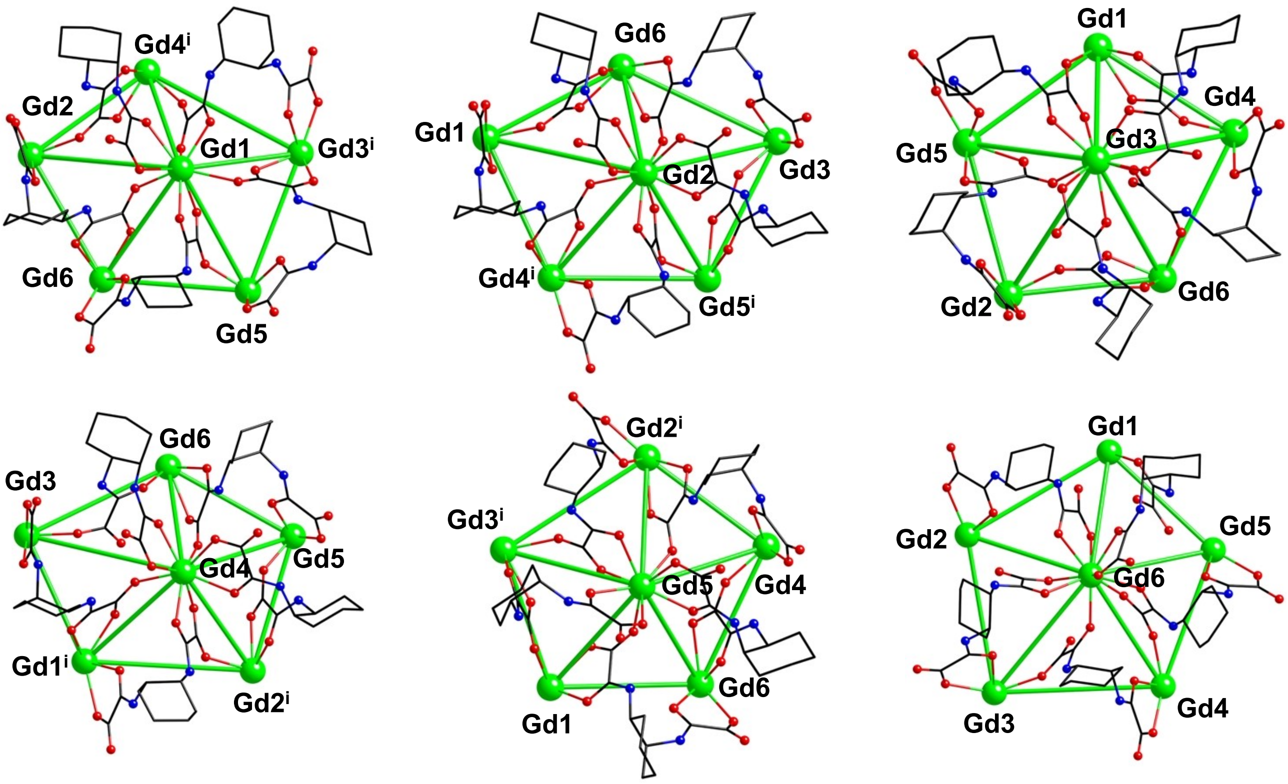


Fig. S5. Five ligands and five adjacent Gd ions linked with each Gd ion. Symmetric code: (i) 1-*x*, 1-*y*, 1-*z*.

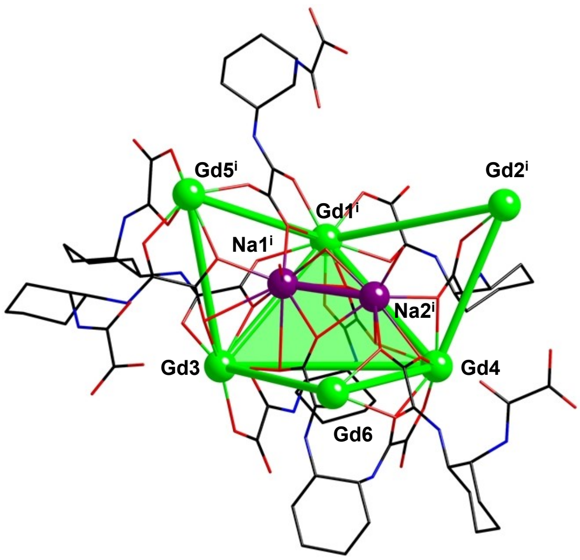


Fig. S6. The linkage between {Na_2} unit and inner wall of {Gd_{12}} icosahedron. Symmetric code: (i) 1-*x*, 1-*y*, 1-*z*.

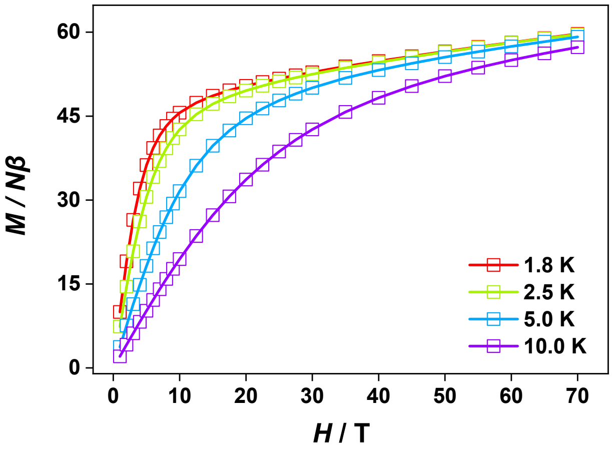


Fig. S7. The *M-H* plot of **Na_4@Dy_{12}@L_{20}** at different temperatures.

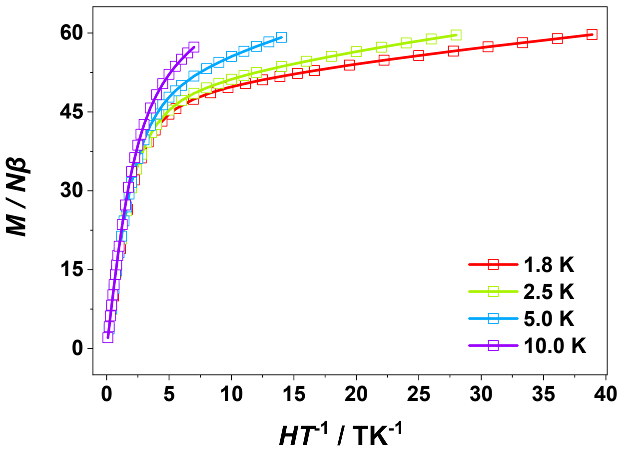


Fig. S8. The *M-HT*$^{-1}$ plot of **Na_4@Dy_{12}@L_{20}** at different temperatures.

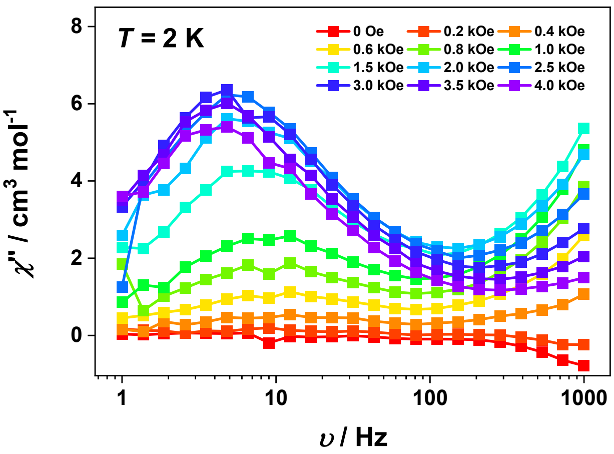


Fig. S9. The χ'' signals of ac susceptibility of **$Na_4@Dy_{12}@L_{20}$** collected under 2 K and different dc fields.

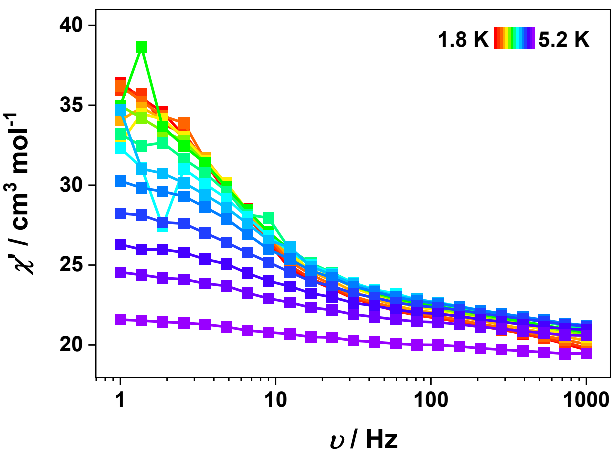


Fig. S10. The χ' signals of ac susceptibility of **$Na_4@Dy_{12}@L_{20}$** collected under 3.0 kOe dc field.

Table S7. The relaxation parameters from the fitting of the Cole-Cole data of $\mathbf{Na_4@Dy_{12}@L_{20}}$.

T/K	χ_s	$\Delta\chi_1$	τ_1	α_1	$\Delta\chi_2$	τ_2	α_2
1.8	2.43214E-14	21.7564	1.48984E-5	0.31071	16.7932	0.03547	0.1664
1.9	8.99314E-6	21.7348	1.27944E-5	0.32247	16.4649	0.03412	0.16771
2	3.13955E-14	22.1812	9.05789E-6	0.39946	15.4576	0.03182	0.14026
2.1	5.18517E-10	22.0681	8.58205E-6	0.36988	15.4473	0.03145	0.1746
2.2	4.54714E-13	22.3189	6.91109E-6	0.3995	14.8628	0.03074	0.17612
2.3	1.15295E-13	22.7179	5.07378E-6	0.459	13.4199	0.02849	0.15165
2.4	2.08061E-5	22.6831	4.75303E-6	0.44792	13.517	0.02878	0.17427
2.6	6.20712E-14	22.652	4.29269E-6	0.42882	11.8657	0.02468	0.18474
2.8	0.06812	22.944	2.88827E-6	0.49403	10.4394	0.02477	0.16902
3	4.78582E-5	23.0675	2.26418E-6	0.51553	9.04835	0.02238	0.16466
3.2	2.24914E-13	22.8471	2.2568E-6	0.49223	8.23834	0.02283	0.18951
3.6	4.64288E-13	22.6017	1.75494E-6	0.49374	6.22817	0.0215	0.19117
4	1.15466E-13	22.2349	1.07579E-6	0.52184	4.47939	0.02091	0.19591
4.4	1.58694E-13	21.6295	7.43594E-7	0.52174	3.29105	0.02177	0.21685
5.2	2.25483E-13	20.2565	1.68706E-7	0.58421	1.5566	0.02217	0.2139

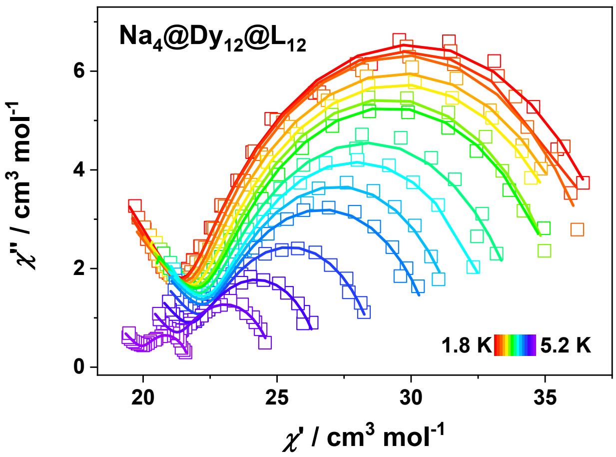


Fig. S11. The Cole-Cole plot of $\mathbf{Na_4@Dy_{12}@L_{20}}$ under 3.0 kOe field.

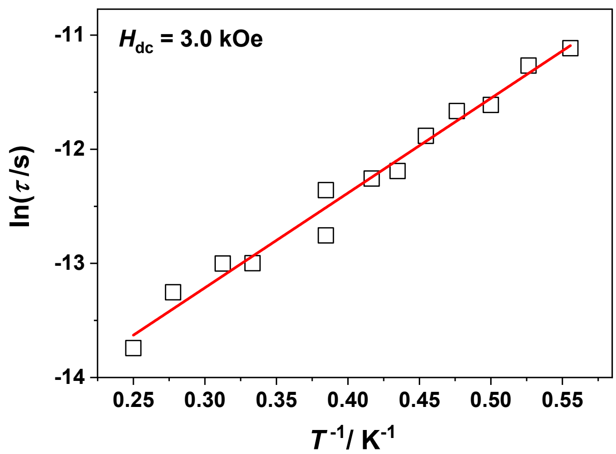


Fig. S12. The Arrhenius fitting to the ln(τ)-T^{-1} data of $\mathbf{Na_4@Dy_{12}@L_{20}}$.

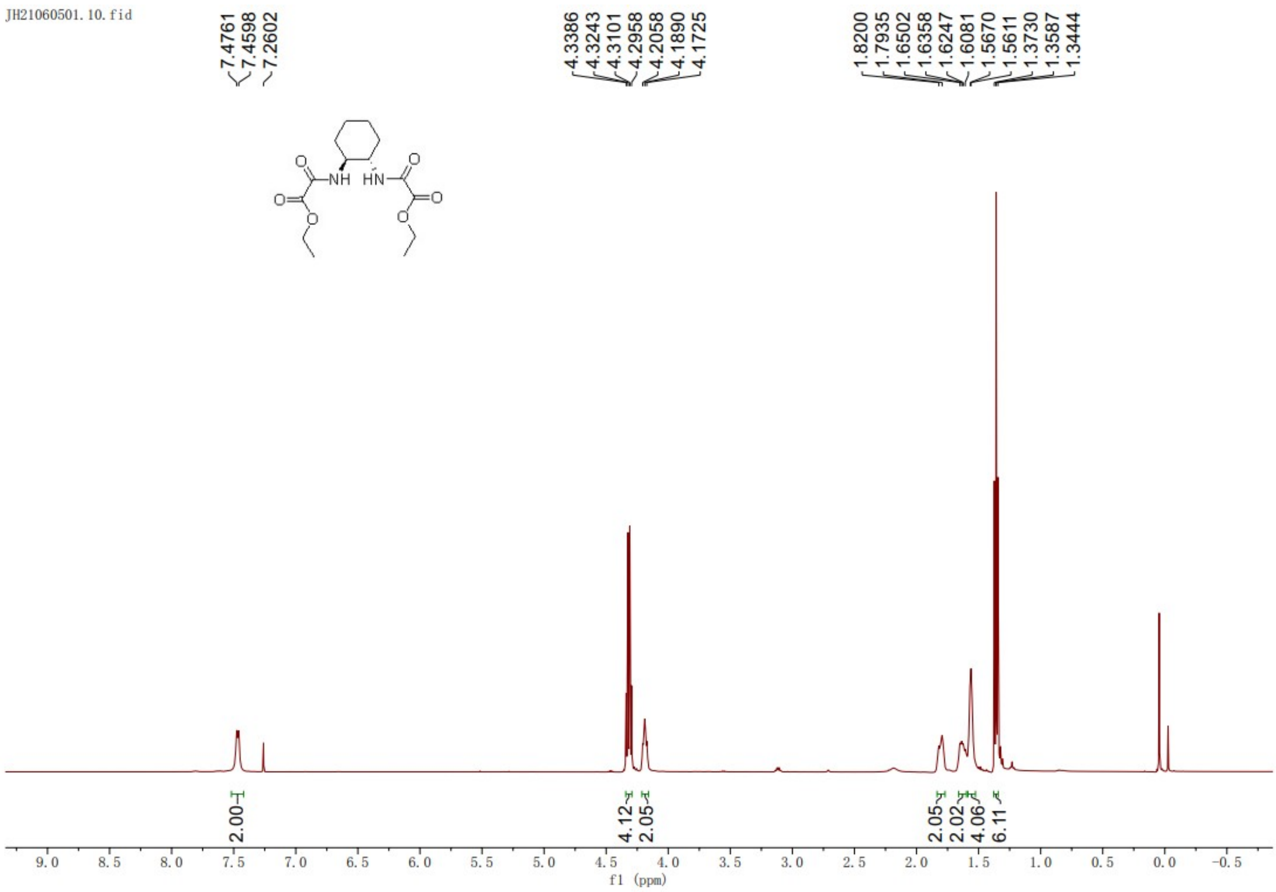


Fig. S13. The [1]HNMR of the $(EtO)_2L$.

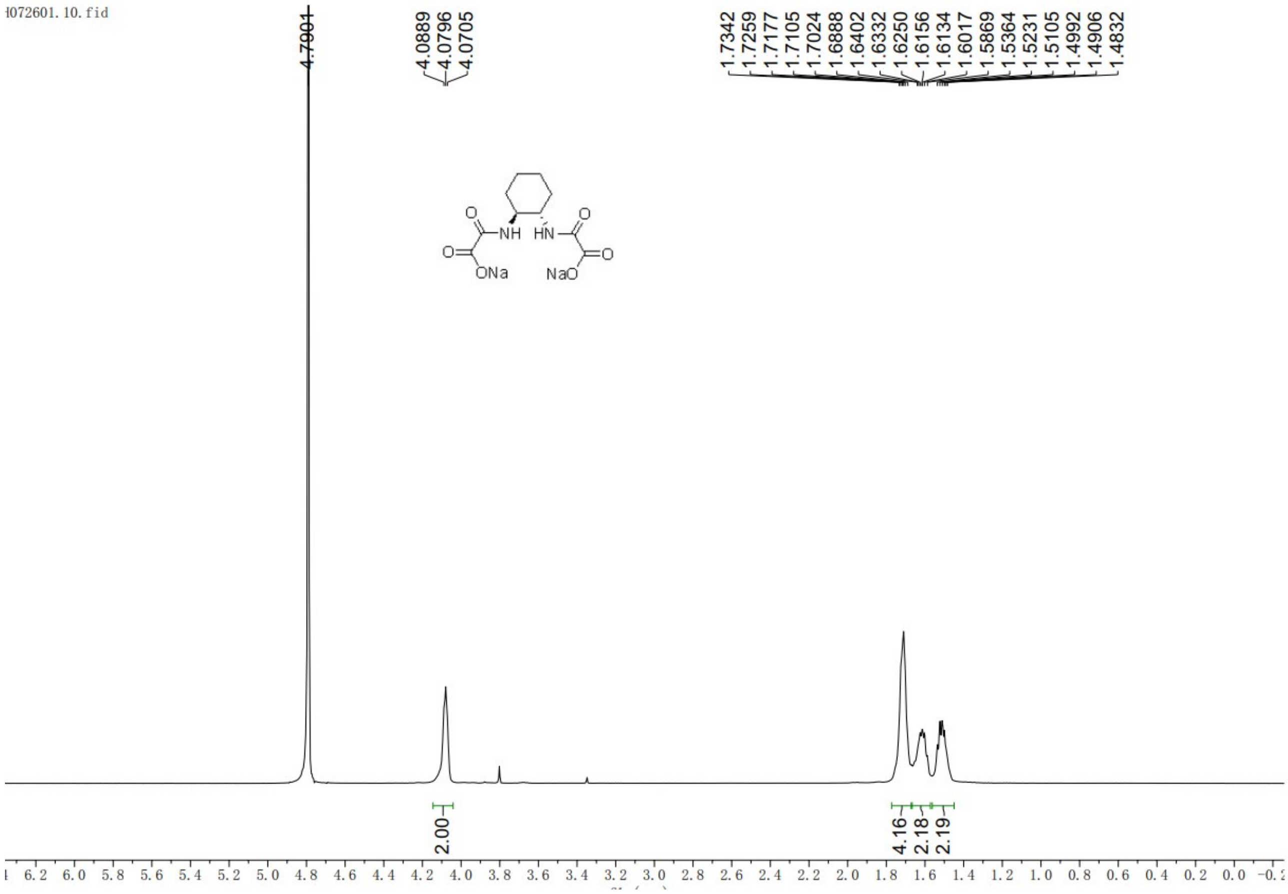


Fig. S14. The ^{1}HNMR of the Na_2L ligand.

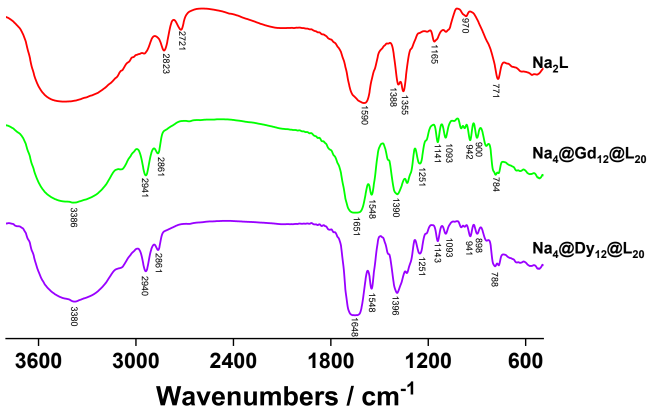
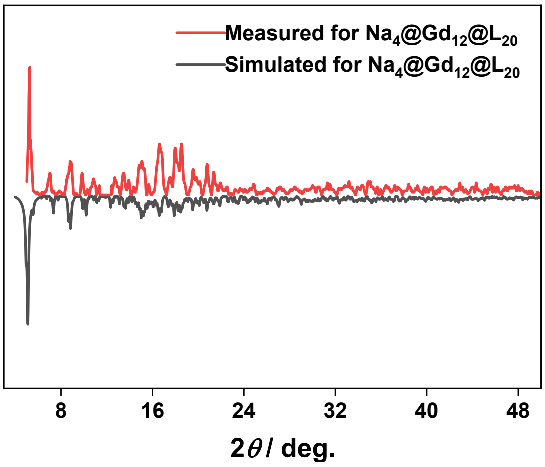


Fig. S15. The IR spectra of the Na_2L ligand, **$Na_4@Gd_{12}@L_{20}$** and **$Na_4@Dy_{12}@L_{20}$**.



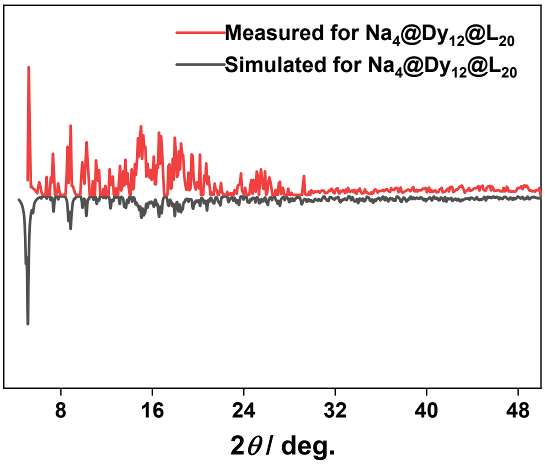
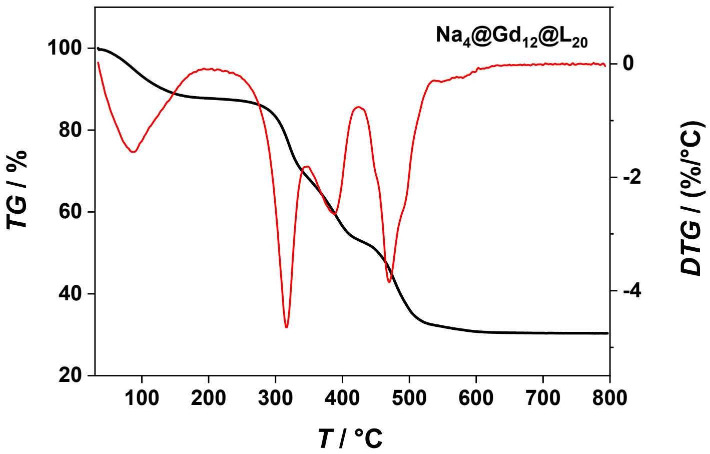


Fig. S16. The PXRD patterners of **Na_4@Gd_{12}@L_{20}** and **Na_4@Dy_{12}@L_{20}**.



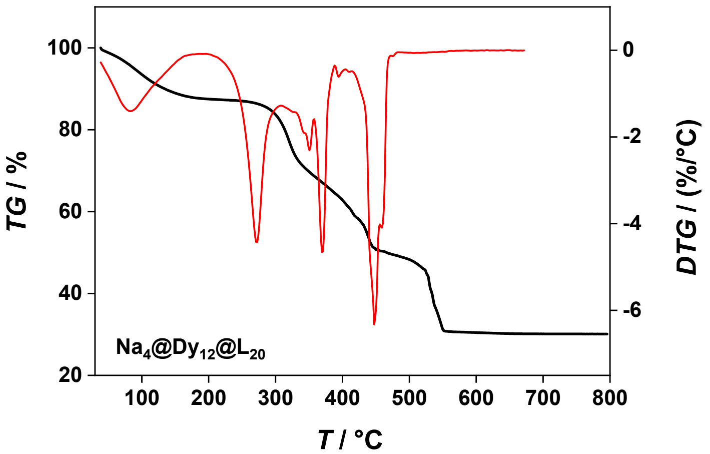


Fig. S17. TG and DTG curves of **$Na_4@Gd_{12}@L_{20}$** and **$Na_4@Dy_{12}@L_{20}$**.

Table S8. Crystal data and structure refinement parameters for **Na_4@Gd_{12}@L_{20}** and **Na_4@Dy_{12}@L_{20}**.

Entries	**Na_4@Gd_{12}@L_{20}**	**Na_4@Dy_{12}@L_{20}**
Empirical formulas	$C_{200}H_{330}Gd_{12}N_{40}Na_4O_{165}$	$C_{202}H_{295}Dy_{12}N_{41}Na_4O_{146}$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a/Å	34.7514(6)	34.5969(3)
b/Å	24.0954(5)	24.0825(2)
c/Å	35.7122(5)	35.6956(3)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	29903.6(9)	29740.9(4)
Z	4	4
ρ_{calc} g/cm^3	1.758	1.714
μ/mm^{-1}	2.74	3.08
F(000)	15768	15192
Reflections collected	82744	89365
Independent reflections	20533	25874
R_{int}	0.062	0.034
Data/restraints/parameters	27310/0/1736	34220/0/1725
Goodness-of-fit on F^2	1.04	1.03
R_1, wR_2 [I>=2(I)][a]	0.0466, 0.0929	0.0375, 0.0797
R_1, wR_2 [all data][b]	0.0664, 0.1055	0.0589, 0.0909

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w(|F_o^2|)^2]^{1/2}$

Table S9. Selected bond lengths and bond angles of **Na_4@Gd_{12}@L_{20}**.

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
Gd1-O2	2.505(4)	Gd3-O12	2.378(5)	Gd5-O11^{i}	2.461(4)
Gd1-O3	2.480(4)	Gd3-O14	2.384(5)	Gd5-O24	2.333(4)
Gd1-O16^{i}	2.391(4)	Gd3-O15	2.420(5)	Gd5-O26	2.402(4)
Gd1-O17^{i}	2.471(4)	Gd3-O28^{i}	2.430(4)	Gd5-O27	2.422(4)
Gd1-O30	2.525(4)	Gd3-O29^{i}	2.459(4)	Gd5-O52	2.382(4)
Gd1-O31	2.357(4)	Gd3-O40	2.501(4)	Gd5-O53	2.427(5)
Gd1-O56	2.469(4)	Gd3-O42	2.404(5)	Gd5-O55	2.286(4)
Gd1-O57	2.418(4)	Gd3-O43	2.263(4)	Gd6-O32	2.410(4)
Gd1-O61	2.442(4)	Gd4-O4^{i}	2.376(4)	Gd6-O33	2.433(4)
Gd2-O6	2.385(4)	Gd4-O5^{i}	2.453(4)	Gd6-O38	2.439(4)
Gd2-O8	2.392(4)	Gd4-O18	2.370(4)	Gd6-O39	2.484(4)
Gd2-O9	2.416(4)	Gd4-O20	2.390(4)	Gd6-O45	2.355(4)
Gd2-O22^{i}	2.385(4)	Gd4-O21	2.480(5)	Gd6-O50	2.570(4)
Gd2-O23^{i}	2.421(4)	Gd4-O46	2.379(4)	Gd6-O51	2.389(4)
Gd2-O34	2.409(4)	Gd4-O47	2.395(4)	Gd6-O58	2.492(4)
Gd2-O35	2.405(5)	Gd4-O49	2.318(4)	Gd6-O59	2.401(4)
Gd2-O37	2.291(4)	Gd5-O10^{i}	2.380(4)		
Bond Angle	**Angle (°)**	**Bond Angle**	**Angle (°)**	**Bond Angle**	**Angle (°)**
O2-Gd1-O30	129.60(14)	O37-Gd2-O34	76.71(15)	O10^{i}-Gd5-O52	137.79(16)
O3-Gd1-O2	64.58(14)	O37-Gd2-O35	143.55(15)	O10^{i}-Gd5-O53	74.16(14)
O3-Gd1-O30	139.34(15)	O12-Gd3-O14	145.98(16)	O24-Gd5-O10^{i}	75.95(15)
O16^{i}-Gd1-O2	117.28(15)	O12-Gd3-O15	144.56(16)	O24-Gd5-O11^{i}	81.29(15)
O16^{i}-Gd1-O3	68.98(15)	O12-Gd3-O28^{i}	81.95(16)	O24-Gd5-O26	145.00(16)
O16^{i}-Gd1-O17^{i}	65.96(14)	O12-Gd3-O29^{i}	74.72(15)	O24-Gd5-O27	143.44(15)
O16^{i}-Gd1-O30	71.55(15)	O12-Gd3-O40	76.88(15)	O24-Gd5-O52	79.13(14)
O16^{i}-Gd1-O56	116.03(14)	O12-Gd3-O42	78.19(17)	O24-Gd5-O53	78.16(16)
O16^{i}-Gd1-O57	144.26(15)	O14-Gd3-O15	66.12(17)	O26-Gd5-O11^{i}	133.56(15)
O16^{i}-Gd1-O61	71.45(16)	O14-Gd3-O28^{i}	127.63(19)	O26-Gd5-O27	66.06(15)

O17^{i}-Gd1-O2	132.37(15)	O14-Gd3-O29^{i}	129.50(17)	O26-Gd5-O53	74.76(16)
O17^{i}-Gd1-O3	75.15(14)	O14-Gd3-O40	69.58(17)	O27-Gd5-O11^{i}	73.80(14)
O17^{i}-Gd1-O30	97.46(14)	O14-Gd3-O42	92.6(2)	O27-Gd5-O53	104.05(16)
O31-Gd1-O2	72.46(15)	O15-Gd3-O28^{i}	80.23(17)	O52-Gd5-O11^{i}	140.88(14)
O31-Gd1-O3	78.23(15)	O15-Gd3-O29^{i}	70.01(16)	O52-Gd5-O26	70.34(15)
O31-Gd1-O16^{i}	134.17(15)	O15-Gd3-O40	134.58(16)	O52-Gd5-O27	136.16(14)
O31-Gd1-O17^{i}	75.47(14)	O28^{i}-Gd3-O29^{i}	64.93(14)	O52-Gd5-O53	67.70(15)
O31-Gd1-O30	139.59(15)	O28^{i}-Gd3-O40	137.88(15)	O53-Gd5-O11^{i}	139.43(14)
O31-Gd1-O56	73.01(15)	O29^{i}-Gd3-O40	139.31(15)	O55-Gd5-O10^{i}	141.54(15)
O31-Gd1-O57	81.49(15)	O42-Gd3-O15	125.40(18)	O55-Gd5-O11^{i}	75.92(15)
O31-Gd1-O61	139.78(16)	O42-Gd3-O28^{i}	74.98(15)	O55-Gd5-O24	109.11(15)
O56-Gd1-O2	126.63(14)	O42-Gd3-O29^{i}	133.92(15)	O55-Gd5-O26	81.90(16)
O56-Gd1-O3	141.78(14)	O42-Gd3-O40	65.32(15)	O55-Gd5-O27	90.49(16)
O56-Gd1-O17^{i}	73.68(14)	O43-Gd3-O12	87.72(18)	O55-Gd5-O52	79.01(16)
O56-Gd1-O30	66.90(14)	O43-Gd3-O14	79.0(2)	O55-Gd5-O53	144.10(15)
O57-Gd1-O2	69.72(15)	O43-Gd3-O15	86.11(19)	O32-Gd6-O33	67.18(14)
O57-Gd1-O3	133.68(15)	O43-Gd3-O28^{i}	139.18(15)	O32-Gd6-O38	70.13(14)
O57-Gd1-O17^{i}	137.83(15)	O43-Gd3-O29^{i}	74.25(14)	O32-Gd6-O39	123.08(14)
O57-Gd1-O30	77.99(15)	O43-Gd3-O40	76.11(16)	O32-Gd6-O50	75.56(14)
O57-Gd1-O56	65.95(14)	O43-Gd3-O42	140.95(16)	O32-Gd6-O58	69.81(14)
O57-Gd1-O61	81.03(17)	O4^{i}-Gd4-O5^{i}	66.61(14)	O33-Gd6-O38	76.17(14)
O61-Gd1-O2	67.54(16)	O4^{i}-Gd4-O20	120.28(17)	O33-Gd6-O39	69.52(14)
O61-Gd1-O3	88.35(16)	O4^{i}-Gd4-O21	72.18(16)	O33-Gd6-O50	142.53(14)
O61-Gd1-O17^{i}	137.36(16)	O4^{i}-Gd4-O46	141.18(15)	O33-Gd6-O58	66.70(14)
O61-Gd1-O30	70.07(16)	O4^{i}-Gd4-O47	78.90(14)	O38-Gd6-O39	65.02(14)
O61-Gd1-O56	129.79(16)	O5^{i}-Gd4-O21	75.45(15)	O38-Gd6-O50	87.93(14)
O6-Gd2-O8	149.60(13)	O18-Gd4-O4^{i}	78.98(15)	O38-Gd6-O58	133.19(15)
O6-Gd2-O9	144.05(15)	O18-Gd4-O5^{i}	75.80(15)	O39-Gd6-O50	133.25(14)
O6-Gd2-O22^{i}	77.96(15)	O18-Gd4-O20	149.23(16)	O39-Gd6-O58	122.02(15)
O6-Gd2-O23^{i}	78.37(14)	O18-Gd4-O21	145.39(15)	O45-Gd6-O32	135.56(14)

O6-Gd2-O34	76.25(14)	O18-Gd4-O46	76.96(15)	O45-Gd6-O33	139.79(14)
O6-Gd2-O35	77.80(15)	O18-Gd4-O47	79.25(15)	O45-Gd6-O38	82.83(14)
O8-Gd2-O9	65.38(14)	O20-Gd4-O5^{i}	132.36(15)	O45-Gd6-O39	70.59(14)
O8-Gd2-O23^{i}	129.04(14)	O20-Gd4-O21	64.87(16)	O45-Gd6-O50	68.67(14)
O8-Gd2-O34	74.14(14)	O20-Gd4-O47	81.41(16)	O45-Gd6-O51	76.47(14)
O8-Gd2-O35	84.64(16)	O46-Gd4-O5^{i}	133.77(15)	O45-Gd6-O58	143.86(14)
O9-Gd2-O23^{i}	74.53(15)	O46-Gd4-O20	73.53(16)	O45-Gd6-O59	90.95(15)
O22^{i}-Gd2-O8	121.61(15)	O46-Gd4-O21	137.59(15)	O51-Gd6-O32	110.29(15)
O22^{i}-Gd2-O9	70.07(16)	O46-Gd4-O47	67.03(15)	O51-Gd6-O33	133.51(14)
O22^{i}-Gd2-O23^{i}	67.33(15)	O47-Gd4-O5^{i}	140.45(14)	O51-Gd6-O38	149.30(14)
O22^{i}-Gd2-O34	138.64(15)	O47-Gd4-O21	112.60(16)	O51-Gd6-O39	126.24(15)
O22^{i}-Gd2-O35	75.88(15)	O49-Gd4-O4^{i}	137.75(15)	O51-Gd6-O50	63.58(14)
O34-Gd2-O9	139.49(15)	O49-Gd4-O5^{i}	71.15(14)	O51-Gd6-O58	69.28(15)
O34-Gd2-O23^{i}	135.89(14)	O49-Gd4-O18	91.80(15)	O51-Gd6-O59	68.11(16)
O35-Gd2-O9	108.82(17)	O49-Gd4-O20	87.91(16)	O58-Gd6-O50	104.44(14)
O35-Gd2-O23^{i}	139.43(15)	O49-Gd4-O21	96.76(16)	O59-Gd6-O32	133.03(15)
O35-Gd2-O34	67.46(15)	O49-Gd4-O46	73.16(15)	O59-Gd6-O33	80.99(16)
O37-Gd2-O6	100.49(15)	O49-Gd4-O47	140.18(15)	O59-Gd6-O38	135.34(15)
O37-Gd2-O8	79.30(16)	O10^{i}-Gd5-O11^{i}	67.07(14)	O59-Gd6-O39	71.19(15)
O37-Gd2-O9	93.87(16)	O10^{i}-Gd5-O26	116.43(16)	O59-Gd6-O50	130.58(16)
O37-Gd2-O22^{i}	140.03(15)	O10^{i}-Gd5-O27	69.91(15)	O59-Gd6-O58	66.13(15)
O37-Gd2-O23^{i}	73.20(15)				

Symmetric code: (i) 1-*x*, 1-*y*, 1-*z*.

Table S10. Selected bond lengths and bond angles of **$Na_4@Dy_{12}@L_{20}$**.

Bond	**Length/Å**	**Bond**	**Length/Å**	**Bond**	**Length/Å**
Dy1-O2	2.502(3)	Dy3-O12	2.354(3)	Dy5-O10^{i}	2.372(3)
Dy1-O3	2.466(3)	Dy3-O14	2.369(4)	Dy5-O11^{i}	2.448(3)
Dy1-O16^{i}	2.379(3)	Dy3-O15	2.397(4)	Dy5-O26	2.386(3)
Dy1-O17^{i}	2.457(3)	Dy3-O28^{i}	2.417(4)	Dy5-O27	2.417(3)
Dy1-O30	2.518(3)	Dy3-O29^{i}	2.445(3)	Dy5-O52	2.371(3)
Dy1-O31	2.338(3)	Dy3-O40	2.485(3)	Dy5-O53	2.409(3)
Dy1-O56	2.451(3)	Dy3-O41	2.382(4)	Dy5-O55	2.274(3)
Dy1-O57	2.395(3)	Dy3-O43	2.253(3)	Dy6-O32	2.398(3)
Dy1-O61	2.414(4)	Dy4-O4^{i}	2.355(3)	Dy6-O33	2.424(3)
Dy2-O6	2.370(3)	Dy4-O5^{i}	2.434(3)	Dy6-O38	2.414(3)
Dy2-O8	2.368(3)	Dy4-O18	2.360(3)	Dy6-O39	2.474(3)
Dy2-O9	2.399(3)	Dy4-O20	2.365(4)	Dy6-O45	2.339(3)
Dy2-O22^{i}	2.371(3)	Dy4-O21	2.478(4)	Dy6-O50	2.567(3)
Dy2-O23^{i}	2.402(3)	Dy4-O46	2.368(3)	Dy6-O51	2.371(3)
Dy2-O34	2.387(3)	Dy4-O47	2.381(3)	Dy6-O58	2.476(3)
Dy2-O35	2.386(4)	Dy4-O49	2.308(3)	Dy6-O59	2.400(3)
Dy2-O37	2.275(3)	Dy5-O24	2.310(3)		

Bond Angle	**Angle (°)**	**Bond Angle**	**Angle (°)**	**Bond Angle**	**Angle (°)**
O2-Dy1-O30	129.45(11)	O37-Dy2-O34	76.51(12)	O24-Dy5-O27	143.38(11)
O3-Dy1-O2	64.69(11)	O37-Dy2-O35	143.68(12)	O24-Dy5-O52	79.34(11)
O3-Dy1-O30	139.03(11)	O12-Dy3-O14	146.65(13)	O24-Dy5-O53	78.78(12)
O16^{i}-Dy1-O2	117.68(12)	O12-Dy3-O15	144.73(12)	O10^{i}-Dy5-O11^{i}	67.38(11)
O16^{i}-Dy1-O3	69.01(12)	O12-Dy3-O28^{i}	82.04(13)	O10^{i}-Dy5-O26	116.35(12)
O16^{i}-Dy1-O17^{i}	66.03(11)	O12-Dy3-O29^{i}	74.46(12)	O10^{i}-Dy5-O27	70.20(12)
O16^{i}-Dy1-O30	71.32(11)	O12-Dy3-O40	76.96(12)	O10^{i}-Dy5-O53	73.84(11)
O16^{i}-Dy1-O56	115.47(11)	O12-Dy3-O41	79.00(13)	O26-Dy5-O11^{i}	133.56(12)
O16^{i}-Dy1-O57	144.35(12)	O14-Dy3-O15	66.37(13)	O26-Dy5-O27	66.17(12)
O16^{i}-Dy1-O61	71.13(13)	O14-Dy3-O28^{i}	125.60(16)	O26-Dy5-O53	74.59(13)

O17^{i}-Dy1-O2	132.07(11)	O14-Dy3-O29^{i}	130.89(14)	O27-Dy5-O11^{i}	73.61(11)
O17^{i}-Dy1-O3	75.03(11)	O14-Dy3-O40	69.84(13)	O52-Dy5-O10^{i}	137.54(12)
O17^{i}-Dy1-O30	97.93(10)	O14-Dy3-O41	90.08(16)	O52-Dy5-O11^{i}	140.85(11)
O31-Dy1-O2	72.60(12)	O15-Dy3-O28^{i}	79.43(14)	O52-Dy5-O26	70.30(12)
O31-Dy1-O3	78.56(12)	O15-Dy3-O29^{i}	70.59(12)	O52-Dy5-O27	136.19(12)
O31-Dy1-O16^{i}	134.11(12)	O15-Dy3-O40	134.84(12)	O52-Dy5-O53	67.82(11)
O31-Dy1-O17^{i}	74.98(11)	O28^{i}-Dy3-O29^{i}	65.45(11)	O53-Dy5-O11^{i}	139.50(10)
O31-Dy1-O30	139.60(12)	O28^{i}-Dy3-O40	138.01(12)	O53-Dy5-O27	104.13(12)
O31-Dy1-O56	73.29(11)	O29^{i}-Dy3-O40	138.77(11)	O55-Dy5-O24	108.79(12)
O31-Dy1-O57	81.46(12)	O41-Dy3-O15	123.69(14)	O55-Dy5-O10^{i}	142.13(11)
O31-Dy1-O61	140.44(13)	O41-Dy3-O28^{i}	74.80(12)	O55-Dy5-O11^{i}	76.17(11)
O56-Dy1-O2	126.76(11)	O41-Dy3-O29^{i}	134.44(12)	O55-Dy5-O26	81.75(13)
O56-Dy1-O3	142.34(11)	O41-Dy3-O40	65.79(12)	O55-Dy5-O27	90.40(13)
O56-Dy1-O17^{i}	73.87(11)	O43-Dy3-O12	89.45(14)	O55-Dy5-O52	78.70(12)
O56-Dy1-O30	66.62(11)	O43-Dy3-O14	79.88(17)	O55-Dy5-O53	143.83(11)
O57-Dy1-O2	69.34(11)	O43-Dy3-O15	85.73(15)	O32-Dy6-O33	67.37(11)
O57-Dy1-O3	133.47(11)	O43-Dy3-O28^{i}	139.79(12)	O32-Dy6-O38	70.02(11)
O57-Dy1-O17^{i}	137.96(11)	O43-Dy3-O29^{i}	74.39(12)	O32-Dy6-O39	123.50(11)
O57-Dy1-O30	78.21(11)	O43-Dy3-O40	76.26(12)	O32-Dy6-O50	75.44(11)
O57-Dy1-O56	66.16(11)	O43-Dy3-O41	141.89(13)	O32-Dy6-O58	69.91(11)
O57-Dy1-O61	81.34(13)	O4^{i}-Dy4-O5^{i}	67.28(11)	O32-Dy6-O59	133.31(12)
O61-Dy1-O2	68.03(12)	O4^{i}-Dy4-O18	79.02(12)	O33-Dy6-O39	69.38(11)
O61-Dy1-O3	88.09(13)	O4^{i}-Dy4-O20	120.16(13)	O33-Dy6-O50	142.56(10)
O61-Dy1-O17^{i}	137.11(12)	O4^{i}-Dy4-O21	73.19(13)	O33-Dy6-O58	66.99(12)
O61-Dy1-O30	69.64(12)	O4^{i}-Dy4-O46	140.23(11)	O38-Dy6-O33	75.93(11)
O61-Dy1-O56	129.42(13)	O4^{i}-Dy4-O47	77.83(11)	O38-Dy6-O39	65.57(11)
O6-Dy2-O9	144.02(11)	O5^{i}-Dy4-O21	74.97(12)	O38-Dy6-O50	87.73(11)
O6-Dy2-O22^{i}	77.93(12)	O18-Dy4-O5^{i}	75.38(11)	O38-Dy6-O58	133.17(12)
O6-Dy2-O23^{i}	78.81(11)	O18-Dy4-O20	149.17(12)	O39-Dy6-O50	133.33(11)
O6-Dy2-O34	76.16(11)	O18-Dy4-O21	145.30(11)	O39-Dy6-O58	121.75(11)

O6-Dy2-O35	77.08(12)	O18-Dy4-O46	76.82(12)	O45-Dy6-O32	135.42(11)
O8-Dy2-O6	149.22(11)	O18-Dy4-O47	79.84(12)	O45-Dy6-O33	139.49(11)
O8-Dy2-O9	65.54(11)	O20-Dy4-O5^i	132.70(12)	O45-Dy6-O38	82.81(11)
O8-Dy2-O22^i	120.98(12)	O20-Dy4-O21	65.22(12)	O45-Dy6-O39	70.50(11)
O8-Dy2-O23^i	129.31(12)	O20-Dy4-O46	73.48(12)	O45-Dy6-O50	68.64(11)
O8-Dy2-O34	74.15(11)	O20-Dy4-O47	81.22(13)	O45-Dy6-O51	76.57(12)
O8-Dy2-O35	84.36(12)	O46-Dy4-O5^i	133.78(12)	O45-Dy6-O58	143.90(11)
O9-Dy2-O23^i	74.41(12)	O46-Dy4-O21	137.68(12)	O45-Dy6-O59	90.80(12)
O22^i-Dy2-O9	70.00(12)	O46-Dy4-O47	67.17(11)	O51-Dy6-O32	110.11(12)
O22^i-Dy2-O23^i	67.91(11)	O47-Dy4-O5^i	140.20(11)	O51-Dy6-O33	133.82(11)
O22^i-Dy2-O34	138.78(12)	O47-Dy4-O21	113.28(13)	O51-Dy6-O38	149.18(11)
O22^i-Dy2-O35	75.48(11)	O49-Dy4-O4^i	138.40(11)	O51-Dy6-O39	125.98(12)
O34-Dy2-O9	139.61(11)	O49-Dy4-O5^i	71.12(11)	O51-Dy6-O50	63.57(11)
O34-Dy2-O23^i	135.44(11)	O49-Dy4-O18	90.68(12)	O51-Dy6-O58	69.26(12)
O35-Dy2-O9	109.10(14)	O49-Dy4-O20	88.51(13)	O51-Dy6-O59	68.28(12)
O35-Dy2-O23^i	139.47(11)	O49-Dy4-O21	96.42(12)	O58-Dy6-O50	104.58(11)
O35-Dy2-O34	67.85(12)	O49-Dy4-O46	73.06(11)	O59-Dy6-O33	81.18(13)
O37-Dy2-O6	101.50(12)	O49-Dy4-O47	140.23(11)	O59-Dy6-O38	135.33(12)
O37-Dy2-O8	79.34(12)	O24-Dy5-O10^i	75.93(11)	O59-Dy6-O39	70.61(12)
O37-Dy2-O9	93.31(13)	O24-Dy5-O11^i	80.95(11)	O59-Dy6-O50	130.67(12)
O37-Dy2-O22^i	140.41(11)	O24-Dy5-O26	145.32(12)	O59-Dy6-O58	66.28(12)
O37-Dy2-O23^i	73.13(11)				

Symmetric code: (i) 1-*x*, 1-*y*, 1-*z*.