Supplementary Materials

Development of Nd (III)-based Terahertz Absorbers Revealing Temperature Dependent Near-infrared Luminescence

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Single-crystal X-ray diffraction (SXRD) studies

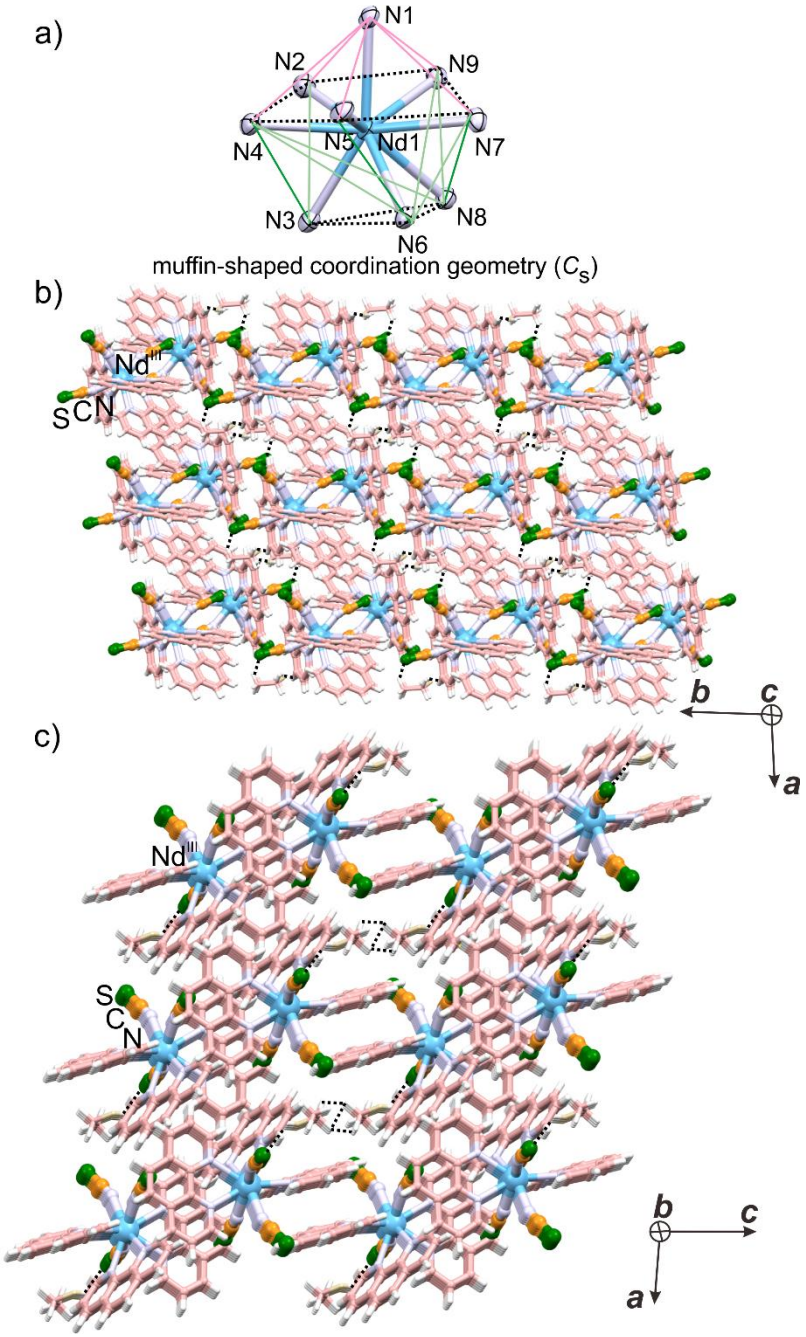


Figure S1. (a) The muffin-shaped coordination geometry of the [NdN_9] moiety, (b, c) the representative crystal packing of **1-S** along *ab*- and *ac*-crystallographic planes with dotted black lines indicating the short contacts with solvent and monomeric Nd(III) unit. The selenium-containing complex **1-Se** has similar crystal packing.

Table S1. Crystal data and structure refinement parameters for **1-S** and **1-Se**.

Compound		1-S	1-Se
Formula		$Nd1C_{39.66}H_{26}N_9O_{0.34}S_3$	$C_{39.66}H_{26}N_9NdO_{0.34}Se_3$
Formula weight [g mol^{-1}]		874.45	1015.15
***T* [K]**		293(2)	293(2)
λ [Å]		0.71073 (Mo Kα)	0.71073 (Mo Kα)
Crystal system		Triclinic	Triclinic
Space group		*P*-1	*P*-1
Unit cell	***a* [Å]**	10.9665(3)	11.1589(15)
	***b* [Å]**	12.2562(2)	12.4218(8)
	***c* [Å]**	15.3925(5)	15.5655(14)
	α [°]	97.193(2)	97.604(6)
	β [°]	101.718(3)	101.155(9)
	γ [°]	101.908(2)	102.185(8)
***V* [Å^3]**		1951.77(9)	2035.1(4)
Z		2	2
Calcd. density		1.488	1.657
Abs. coefficient		1.533	3.999
***F*(000)**		875.0	983.0
Crystal size [mm^3]		0.32 × 0.1 × 0.04	0.12 × 0.04 × 0.02
Crystal morphology		needle	needle
2Θ range [°]		3.45 to 54.792	3.836 to 54.898
Limiting indices		-14 < *h* < 14 -15< *k* < 15 -19 < *l* < 19	-14 < *h* < 14 -16< *k* < 15 -19 < *l* < 19
Collected refls		39779	37870
Unique refls		8210	8503
***R*$_{int}$**		0.0615	0.1893
Completeness		100%	100%
Data/restraints/parameters		8210/12/498	8503/24/492
GOF on *F*^{2}		1.034	1.043
Final *R* values		R_1 = 0.0496 [I>2σ(I)] wR_2 = 0.1325 [all]	R_1 = 0.1338 [I>2σ(I)] wR_2 = 0.3365 [all]
Largest diffr. peak/hole		2.27/-0.64 e·A^{-3}	2.79/-1.41 e·A^{-3}

Table S2. Selected distances and angles of **1-S** and **1-Se**.

Parameter	Distance [Å]		Parameter	Distance [Å]	
	1-S	1-Se	1-S	1-S	1-Se
Nd1–N1$_{(XCN)}$	2.500(4)	2.500(16)	**Nd1–N4**$_{(phen)}$	2.686(4)	2.674(15)
Nd1–N2$_{(XCN)}$	2.489(4)	2.49(2)	**Nd1–N5**$_{(phen)}$	2.714(4)	2.692(16)
Nd1–N3$_{(XCN)}$	2.535(4)	2.543(14)	**Nd1–N6**$_{(phen)}$	2.660(3)	2.643(13)
			Nd1–N7$_{(phen)}$	2.665(4)	2.653(15)
			Nd1–N8$_{(phen)}$	2.706(3)	2.703(13)
			Nd1–N9$_{(phen)}$	2.708(4)	2.699(14)
Parameter	**Angle [°]**		**Parameter**	**Angle [°]**	
	1-S	**1-Se**	**1-S**	**1-S**	**1-Se**
N1–Nd1–N3	151.08(14)	151.0(5)	**N6–Nd1–N4**	100.37(11)	135.7(5)
N1–Nd1–N4	69.97(12)	69.7(5)	**N6–Nd1–N5**	65.99(11)	137.1(5)
N1–Nd1–N5	107.44(13)	108.2(5)	**N6–Nd1–N7**	61.35(11)	99.6(5)
N1–Nd1–N6	75.83(12)	75.6(5)	**N6–Nd1–N8**	69.83(11)	67.7(4)
N1–Nd1–N7	129.77(12)	130.3(5)	**N6–Nd1–N9**	120.62(11)	62.3(5)
N1–Nd1–N8	73.38(12)	72.6(4)	**N7–Nd1–N4**	139.27(12)	70.0(4)
N1–Nd1–N9	115.18(13)	114.7(5)	**N7–Nd1–N5**	79.04(12)	121.4(5)
N2–Nd1–N1	79.40(14)	78.3(5)	**N7–Nd1–N8**	68.31(11)	139.3(5)
N2–Nd1–N3	80.18(14)	81.1(5)	**N7–Nd1–N9**	71.37(11)	80.0(5)
N2–Nd1–N4	72.86(13)	73.6(5)	**N8–Nd1–N5**	133.77(11)	69.2(5)
N2–Nd1–N5	125.03(13)	124.4(5)	**N8–Nd1–N9**	60.35(11)	71.6(5)
N2–Nd1–N6	155.11(13)	153.7(5)	**N9–Nd1–N5**	137.23(11)	60.9(4)
N2–Nd1–N7	138.26(13)	138.1(5)	**C1–N1–Nd1**	159.2(4)	160.9(14)
N2–Nd1–N8	100.91(13)	99.6(5)	**N1–C1–S1**	177.9(4)	—
N2–Nd1–N9	68.65(13)	68.0(5)	**N2–C2–S2**	179.4(5)	—
N3–Nd1–N4	84.56(12)	84.9(5)	**N3–C3–S3**	177.4(6)	—
N3–Nd1–N5	68.93(12)	67.8(5)	**N1–C1–Se1**	—	177.2(15)
N3–Nd1–N6	123.70(12)	124.2(5)	**N2–C2–Se2**	—	179(2)
N3–Nd1–N7	78.68(13)	78.3(5)	**N3–C3–Se3**	—	174(2)
N3–Nd1–N8	130.86(12)	131.4(5)	**C2–N2–Nd1**	159.1(4)	159.4(16)
N3–Nd1–N9	75.39(12)	75.3(4)	**C3–N3–Nd1**	164.3(4)	163.0(18)
N4–Nd1–N5	60.28(12)	59.3(5)			
N4–Nd1–N8	143.35(11)	142.4(5)			
N4–Nd1–N9	138.92(12)	138.8(5)			

Table S3. Results of Continuous Shape Measure (CSM) analyses for the first coordination sphere of Nd(III) ion of **1-S** and **1-Se**.

Compound	Nd^{III} center (CSM parameters)				
	$S_{JCSAPR-9}$	$S_{CSAPR-9}$	$S_{JTCTPR-9}$	$S_{TCTPR-9}$	S_{MFF-9}
Ideal JCSAPR-9	0	1.133	2.359	2.314	2.135
Ideal CSAPR-9	1.133	0	2.924	1.169	0.817
Ideal JTCTPR-9	2.359	2.924	0	2.625	3.805
Ideal TCTPR-9	2.314	1.169	2.625	0	2.045
Ideal MFF-9	2.135	0.817	3.805	2.045	0
1-S	2.546	1.715	4.019	1.878	1.502
1-Se	2.55	1.687	3.924	1.878	1.385

*CSM parameters[5]: $S_{JCSAPR-9}$ - the parameter related to the capped square antiprism geometry (C_{4v} symmetry), $S_{CSAPR-9}$ - the parameter related to the spherical capped square antiprism geometry (C_{4v} symmetry), $S_{JTCTPR-9}$ - the parameter related to the tricapped trigonal prism geometry (D_{3h} symmetry), $S_{TCTPR-9}$ - the parameter related to the spherical tricapped trigonal prism geometry (D_{3h} symmetry), S_{MFF-9} - the parameter related to the muffin geometry (C_s symmetry), $S = 0$ for the ideal geometry and increases with the increasing distortion from the ideal polyhedron.

Thermogravimetric analysis

The partially occupied ethanol molecules are removed from the crystal structure by 50°C in both assemblies as indicated in the TGA patterns. **1-S** shows higher stability until 250°C followed by the decomposition of three phen and three thiocyanate ligands, which account for 74% of the weight loss. On the other hand, **1-Se** begins to decompose above 180°C due to the less stable selenocyanate which decomposes to selenium and free cyanide. A further increase in temperature leads to the elimination of three cyanide and three phen, which corresponds to 58% of mass loss. These results are in agreement with those of the powder diffraction and single-crystal studies.

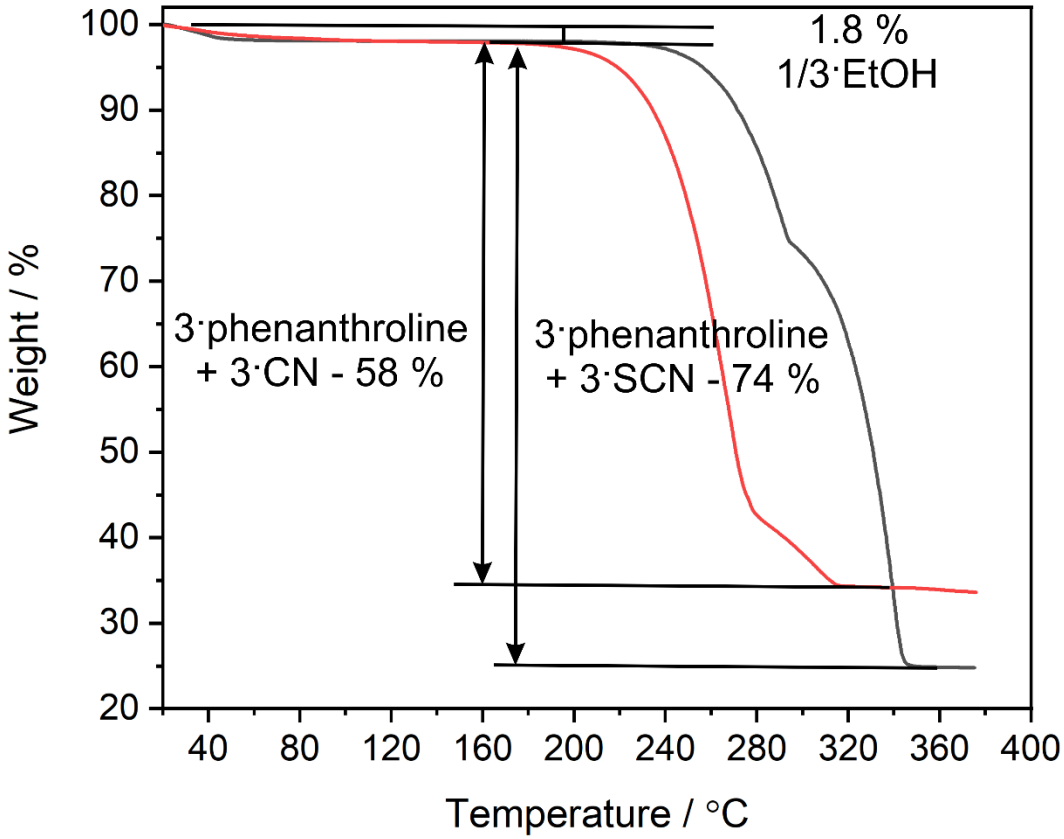


Figure S2. Thermogravimetric plots for **1-S** and **1-Se** with indicated weight losses.

Powder X-ray diffraction (PXRD) studies

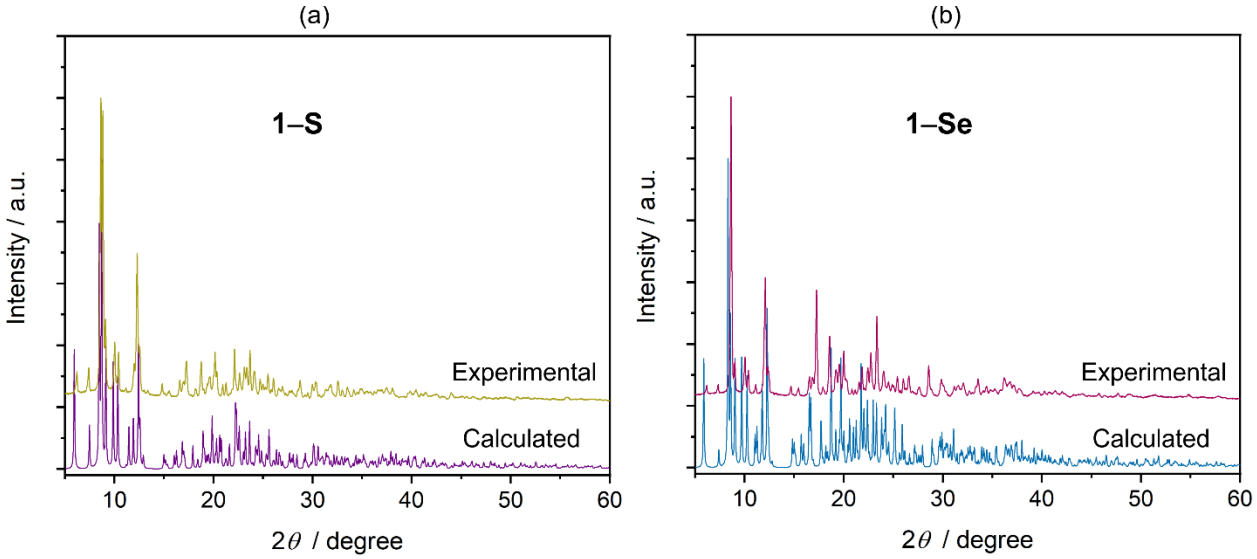


Figure S3. (a, b) Experimental and calculated powder X-ray diffraction patterns of **1**-**S** and **1**-**Se**. The calculated PXRD patterns were simulated based on the structures determined in the SXRD experiments at 300 K.

Vibrational spectroscopy

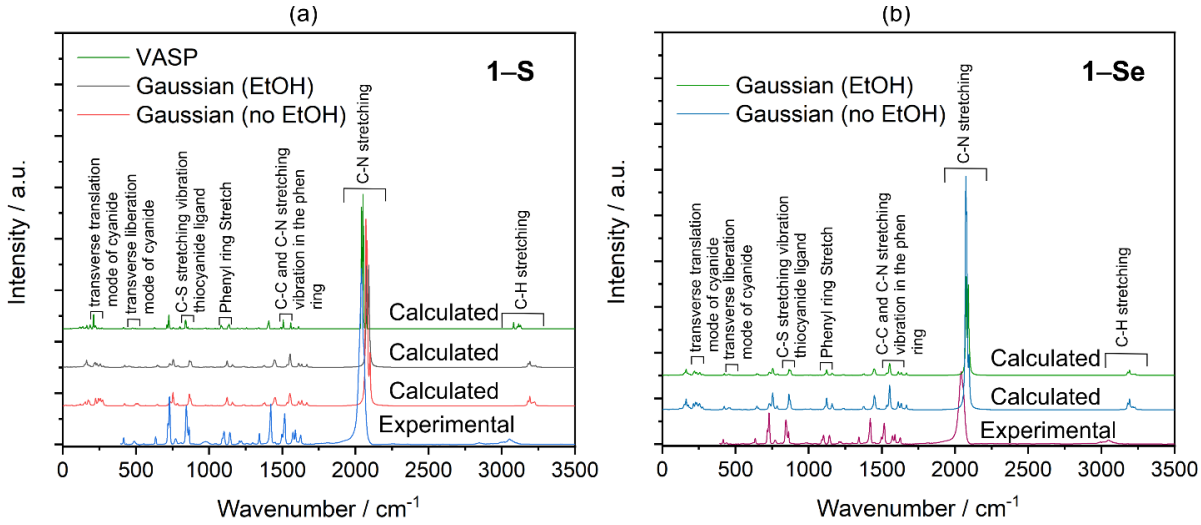


Figure S4. (a, b) Infrared (IR) absorption spectra in KBr matrix with assignment for **1**-**S** and **1**-**Se** compared with calculated IR spectra. DFT calculations were performed using Gaussian 16 for two models with and without ethanol. Panel (a) is supplemented by IR spectra determined from first-principal phonon calculation using VASP.

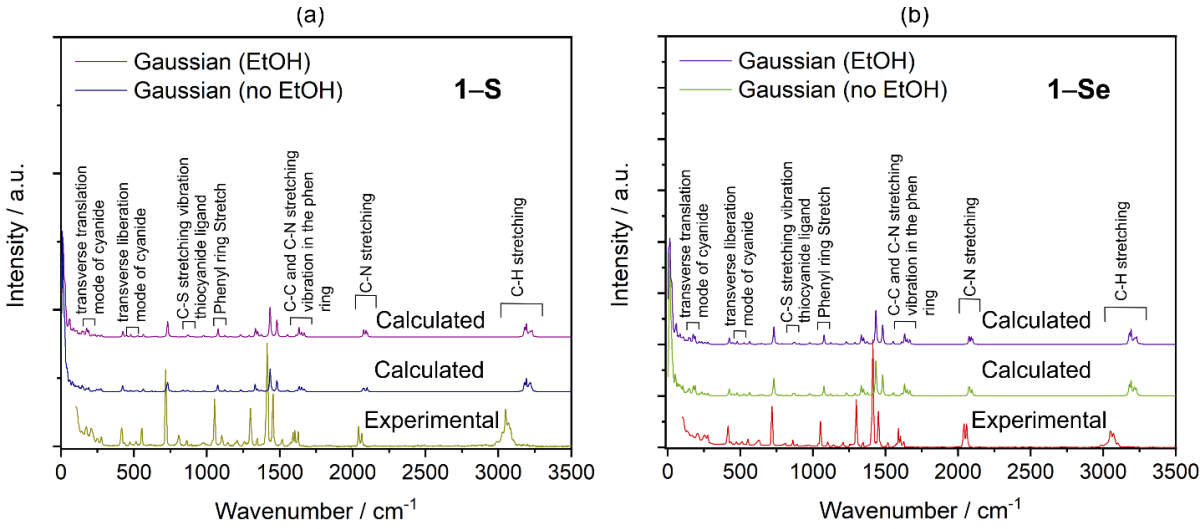


Figure S5. (a, b) Experimental Raman scattering spectra for single crystals with assignment for **1-S** and **1-Se** compared with calculated Raman spectra. DFT calculations were performed using Gaussian 16 for two models with and without ethanol in the input.

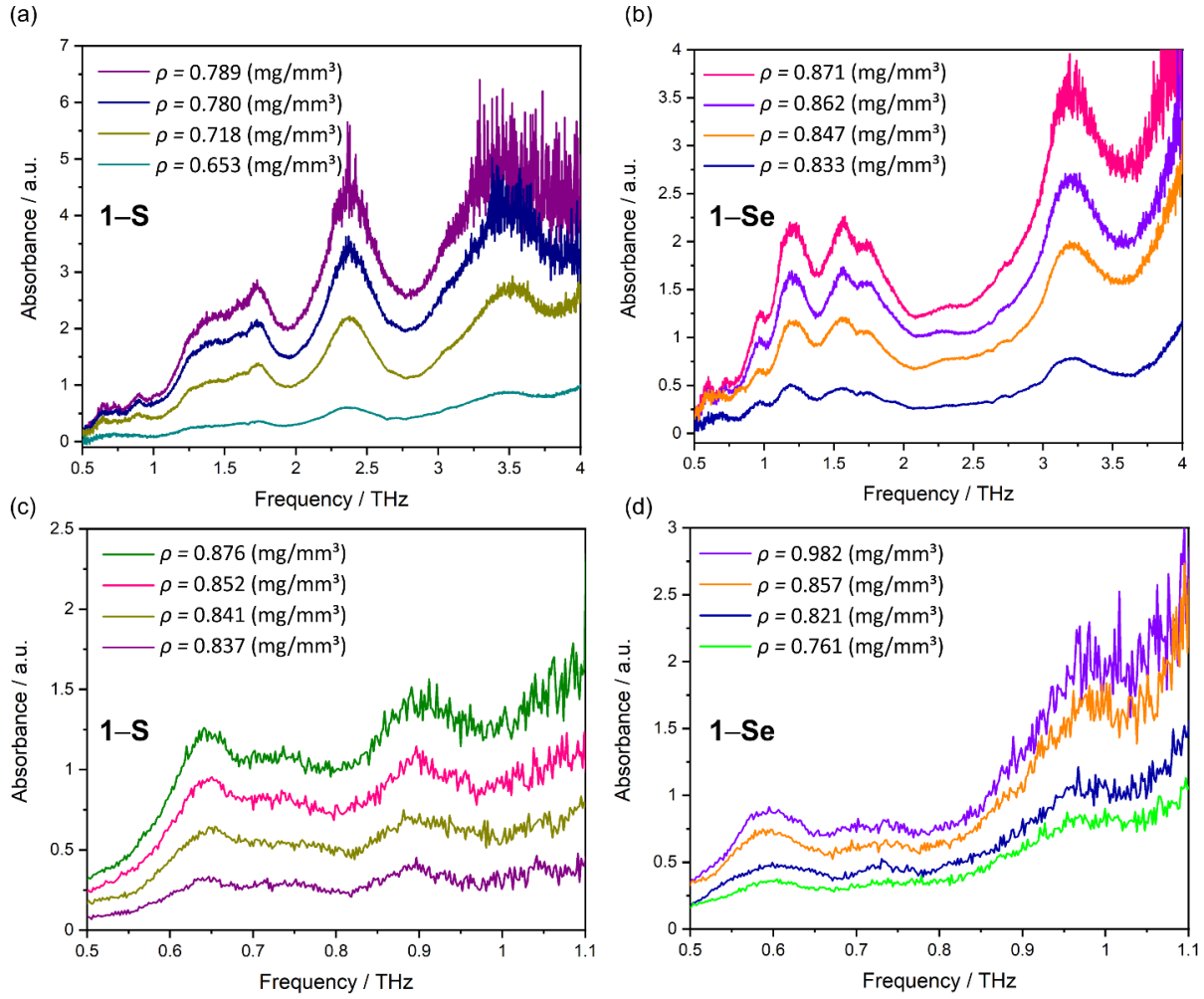


Figure S6. THz-TDS spectra of (a, c) **1-S** and (b, d) **1-Se** measured with two different measurement modules for different fill rates (ρ).

Table S4. List of IR and Raman active vibrational modes for **1-S** and **1-Se** without ethanol solvent, including relevant assignment.

Mode #	*f* (cm^{-1})	IR (KM/Mole)	Raman activity ($Å^4$/amu)	Mode#	*f* (cm^{-1})	IR (KM/Mole)	Raman activity ($Å^4$/amu)	Assignment
	1-S without EtOH				**1-Se** without EtOH			
1	7.4249	466.9135	16.53137	**1**	7.3847	454.9772	3.9382482863	
2	9.7835	462.1234	16.79887	**2**	12.1978	78.03622	15.2320949205	
3	15.6492	462.2074	6.162452	**3**	13.552	416.9262	4.7206835380	
4	17.9413	107.3768	7.09294	**4**	15.6588	195.74	6.2201452692	
5	21.1039	594.0268	3.382326	**5**	19.9346	262.9633	4.4750779374	
6	25.6796	221.2845	9.050351	**6**	23.9066	300.1068	5.5863735052	
7	33.9624	85.32666	1.568453	**7**	27.1271	171.2257	3.0406012640	
8	38.6337	189.3414	0.543075	**8**	32.8149	148.185	1.3415765093	
9	41.2238	10.28709	1.928389	**9**	34.6902	82.2255	1.5812744187	
10	44.8882	205.2902	1.418854	**10**	38.1421	3.409732	0.7546622257	
11	55.6678	2.809243	0.823534	**11**	50.379	71.48274	2.4504278637	
12	58.4369	74.15321	0.38073	**12**	55.1518	123.2875	1.4369017055	
13	60.8209	219.8006	0.495854	**13**	60.0222	93.02492	0.4610260628	
14	63.9928	107.0775	0.824484	**14**	69.6821	228.9999	1.5745973789	
15	75.8287	20.26562	1.197572	**15**	76.7394	80.51118	0.4831503758	
16	79.4608	17.38629	0.690252	**16**	80.8846	27.83739	1.0888683932	
17	86.7235	24.76712	0.198563	**17**	87.0884	6.917098	0.6153951062	
18	87.6824	19.86909	0.759092	**18**	89.9065	54.14805	0.5295425442	
19	97.6339	213.1298	0.769898	**19**	93.4713	70.81968	0.4156185566	
20	103.6875	8.037469	0.343079	**20**	96.1063	34.76069	0.2172053487	
21	108.4964	86.02309	0.420631	**21**	104.0772	34.12621	0.8894711951	
22	113.4303	110.59	0.306284	**22**	105.3774	8.733884	0.7257534061	
23	118.5026	87.51906	0.43156	**23**	116.9033	116.1397	0.0770180125	
24	119.1857	338.9821	0.209063	**24**	118.7883	156.6429	0.2937461598	
25	121.9015	56.38104	0.300364	**25**	126.4428	46.1465	0.1620397736	
26	131.3398	46.37902	0.521183	**26**	133.0581	134.411	0.4719722177	
27	143.1833	149.6059	0.49312	**27**	142.771	107.6574	0.9087139621	
28	145.7013	380.6459	0.725948	**28**	147.0104	411.9291	0.2947927050	Movement of phen ligand perpendicular to the aromatic ring
29	152.5344	155.3029	0.456788	**29**	151.8817	518.7866	0.9250059937	
30	154.2134	585.8627	0.175142	**30**	162.3673	1534.441	0.1076032368	

31	173.0555	1004.176	0.59161	**31**	174.1478	215.5928	1.3200130957	
32	180.6065	640.0013	0.273035	**32**	178.4827	428.467	0.8521814517	
33	189.2682	69.83989	0.824176	**33**	188.9784	181.6692	1.7580235258	
34	224.0001	1094.439	0.191808	**34**	212.3844	649.3653	0.2776395142	Transverse translation mode of cyanide
35	235.5061	90.96946	0.01826	**35**	226.1299	668.5882	0.3524575287	
36	236.9594	7.225919	0.090079	**36**	234.5683	449.7829	0.5738620946	
37	243.7726	825.4775	0.395265	**37**	238.6361	225.9486	0.1674487832	
38	250.0233	279.6945	0.058383	**38**	248.4767	278.539	0.0970167824	
39	251.6026	12.25823	0.159744	**39**	253.485	170.7122	0.1703220091	
40	257.3856	482.5596	0.136873	**40**	254.8022	226.5623	0.2057698040	
41	259.0093	343.7536	0.219818	**41**	256.9626	126.5335	0.0639895909	
42	269.7581	380.5246	0.159135	**42**	262.9795	120.65	0.1107497968	Movement of phen ligand along aromatic ring (ring stretch)
43	272.4776	210.454	0.145779	**43**	275.1005	76.03914	0.2144855214	
44	273.5108	96.78465	0.281089	**44**	275.4573	108.8557	0.0673308124	
45	275.7876	160.3758	0.221647	**45**	276.2837	19.67815	0.2578155243	
46	417.9551	3.393261	0.062525	**46**	420.7954	39.044	0.1301512948	
47	419.8142	21.55038	0.218134	**47**	421.5903	57.4776	0.3645266317	
48	421.4527	35.11821	0.233909	**48**	422.1799	70.76462	0.4642178063	
49	421.5812	83.86341	0.549873	**49**	423.7286	45.46683	0.1659391694	
50	424.0801	46.01428	0.355529	**50**	424.5498	7.818114	0.3404444617	
51	425.05	17.29975	0.252708	**51**	426.4382	5.646774	0.1688734891	
52	442.4367	14.05731	0.135231	**52**	443.5971	10.9943	0.0747767675	
53	448.6842	3.820603	0.091636	**53**	444.3116	2.872327	0.1880735695	
54	449.9368	6.711109	0.111385	**54**	446.5061	12.71229	0.0284329389	

55	474.3522	3.104205	0.086564	**55**	449.1756	30.35819	0.0753042535	
56	476.5471	4.078578	0.148591	**56**	450.7264	5.638998	0.1053586873	
57	477.0303	3.57434	0.073215	**57**	453.067	48.25665	0.0122488099	
58	494.8747	5.292328	0.011156	**58**	454.4659	26.71648	0.0809301109	Transverse liberation mode of cyanide
59	495.9401	59.23764	0.021044	**59**	459.6967	44.43736	0.0746112222	
60	500.4711	25.14302	0.024852	**60**	464.0461	65.02158	0.0397568033	
61	501.3931	86.50762	0.006792	**61**	475.6187	8.658732	0.1958009677	
62	509.5946	65.36543	0.048787	**62**	476.9125	9.969468	0.3032278944	
63	512.4422	76.08736	0.087673	**63**	478.9735	2.290491	0.2125199477	
64	515.8621	0.128375	0.067252	**64**	516.6626	3.369652	0.1103476474	
65	516.736	52.05619	0.081718	**65**	521.6282	10.18174	0.0978083914	Various motions related to the perpendicular and parallel stretching of phen aromatic rings. Some motions also related to the slant movement of rings
66	521.5709	7.670228	0.053003	**66**	523.0544	5.848474	0.0819395398	
67	523.4271	3.864957	0.036599	**67**	524.3397	5.694143	0.0653227884	
68	524.5903	2.962825	0.086073	**68**	525.5708	3.373262	0.0435160129	
69	525.3042	1.906967	0.055293	**69**	526.507	9.697933	0.1719935599	
70	559.9303	0.751668	0.049176	**70**	559.1528	2.736878	0.0334136046	
71	561.6104	0.961103	0.054507	**71**	562.6026	0.382203	0.1095201497	
72	563.046	2.037048	0.239026	**72**	563.436	1.210762	0.3072984777	
73	563.6739	0.036095	0.277017	**73**	564.1764	6.775612	0.1397759712	
74	564.1134	16.46851	0.060884	**74**	565.0924	7.19739	0.1298242855	
75	565.8075	1.323436	0.05755	**75**	567.3454	2.980031	0.0933231189	
76	618.9055	1.229231	0.09056	**76**	620.5252	0.480251	0.0469522282	
77	620.7227	0.712114	0.069427	**77**	622.9342	4.32732	0.0693671358	
78	623.3492	2.474217	0.021592	**78**	624.6482	4.183882	0.0607108496	
79	638.9163	23.06161	0.015303	**79**	636.2264	23.16225	0.0687101390	

80	645.0785	40.2373	0.047258	**80**	642.2029	34.61417	0.0115918647	
81	647.6287	44.71734	0.033342	**81**	645.5904	2.941421	0.1430987516	
82	723.9932	47.51836	0.701754	**82**	645.9121	56.34586	0.1015327556	
83	729.204	97.59855	0.90287	**83**	647.7679	65.77227	0.0311509451	
84	731.9271	71.64025	1.473149	**84**	657.6545	47.47936	0.0876390790	
85	735.9896	21.29317	0.007797	**85**	726.6234	62.96303	0.8829484827	
86	736.7835	31.81627	0.013298	**86**	729.3674	96.75241	1.2173721583	
87	738.1455	34.37826	0.018494	**87**	731.899	44.80243	2.5241081040	
88	752.7637	226.9058	0.040834	**88**	736.246	36.87551	0.0181639796	
89	752.8044	334.648	0.039486	**89**	736.7352	26.47432	0.0346083157	
90	755.7492	55.04134	0.017925	**90**	737.2089	36.83384	0.0301430531	
91	781.9715	21.45629	0.004991	**91**	751.5352	202.947	0.0750516303	
92	782.6904	79.1676	0.033384	**92**	754.0346	210.2967	0.0408700505	
93	783.8418	5.148074	0.011764	**93**	755.6542	235.3539	0.0210214462	
94	816.4251	2.087968	0.027514	**94**	781.5068	21.47313	0.0338141904	
95	818.5273	7.513561	0.030188	**95**	783.3687	35.0148	0.0792409098	
96	819.6307	7.094106	0.030172	**96**	784.5092	62.29438	0.0758853025	
97	835.2359	7.891522	0.083497	**97**	814.5299	5.910165	0.0267021669	C–S stretching vibration from thiocyanate ligand
98	836.0269	3.957298	0.273055	**98**	817.3071	2.44936	0.1860799625	
99	843.8778	10.76962	0.135666	**99**	818.9019	2.595611	0.0206638772	
100	861.771	13.75412	0.030579	**100**	861.8109	4.673989	0.0748959858	
101	862.9746	49.25502	0.075057	**101**	863.287	64.56978	0.0761192105	
102	863.887	196.9709	0.049735	**102**	863.4618	11.2512	0.1058963665	
103	864.124	66.18541	0.049491	**103**	864.6956	202.5745	0.1510994807	
104	865.5799	50.92684	0.06557	**104**	865.195	79.2291	0.0463353675	
105	866.6161	75.13333	0.024975	**105**	866.0929	82.26582	0.0955487597	

106	870.5185	50.04674	0.077741	**106**	872.1529	43.25176	0.2135150871	
107	873.1257	71.05725	0.132314	**107**	873.3524	63.55291	0.2564336884	
108	875.0379	117.2923	0.055948	**108**	874.4471	94.38541	0.0681922237	
109	898.1086	0.943925	0.029533	**109**	900.8644	0.097425	0.0395905159	
110	903.1393	1.913997	0.070155	**110**	903.4979	1.997573	0.0652756539	
111	905.1613	2.596833	0.113434	**111**	904.5079	3.614905	0.1130485673	
112	967.7616	4.473925	0.023523	**112**	962.8913	13.49422	0.1281394490	
113	973.4537	13.72893	0.15034	**113**	974.8209	16.1545	0.3646205604	C–H motion of the phen ligand in various directions above the aromatic ring
114	976.7662	6.737038	0.021012	**114**	978.1832	1.38053	0.1837740639	
115	983.623	0.551997	0.012406	**115**	980.5889	3.112302	0.0449037592	
116	984.0917	0.362418	0.018204	**116**	982.7941	2.664485	0.0705887449	
117	984.2792	2.416873	0.030801	**117**	985.6859	2.552247	0.0508044943	
118	991.4072	1.276807	0.021591	**118**	989.4026	3.216831	0.0148402634	
119	992.9519	2.459645	0.01114	**119**	991.0183	0.157399	0.0781764503	
120	993.4476	3.554706	0.008737	**120**	994.0734	6.761409	0.0395701085	
121	1004.839	2.364642	0.003189	**121**	1003.625	2.705378	0.0148903155	
122	1009.341	7.181651	0.017164	**122**	1009.096	7.75506	0.0291096292	
123	1010.139	0.095969	0.003535	**123**	1010.228	10.35982	0.0082383498	
124	1014.374	6.78144	0.004613	**124**	1012.601	2.775163	0.0389975997	
125	1019.231	7.272443	0.013205	**125**	1014.781	7.551222	0.0100935065	
126	1023.147	1.741748	0.011369	**126**	1020.074	7.753729	0.0376575351	
127	1054.49	2.669839	0.007431	**127**	1055.095	2.262219	0.0183947240	Phenyl–ring breathing vibration of phenanthroline ligands
128	1054.659	0.687306	0.027959	**128**	1056.114	4.122312	0.0463231708	
129	1056.388	6.935453	0.025545	**129**	1056.202	3.514227	0.0404872668	
130	1071.187	3.252039	0.349177	**130**	1073.756	3.216394	0.6853416142	

131	1074.541	1.687401	0.201605	**131**	1075.185	1.53315	0.7208182882	
132	1074.867	1.101581	1.428968	**132**	1076.764	2.984367	1.1151782326	
133	1104.115	8.052394	0.006382	**133**	1106.861	9.242364	0.0148935388	
134	1107.543	17.18527	0.013291	**134**	1108.654	15.24649	0.0415003675	
135	1108.388	12.89801	0.024584	**135**	1110.075	20.68632	0.0108200445	
136	1117.418	64.08994	0.075986	**136**	1120.527	68.87586	0.0577342813	Phenyl ring stretch
137	1121.612	118.7186	0.171205	**137**	1123.002	207.097	0.1165231201	
138	1123.68	138.0285	0.3	**138**	1123.399	6.860182	0.3057141313	
139	1157.224	29.08628	0.04869	**139**	1158.4	46.97839	0.0391957345	
140	1157.792	43.3782	0.044898	**140**	1158.98	37.84623	0.0557387667	
141	1159.918	39.37849	0.050406	**141**	1159.67	41.55006	0.0492542923	
142	1165.215	7.31243	0.033919	**142**	1166.701	15.87038	0.0532300013	
143	1165.791	9.277187	0.035001	**143**	1166.814	10.15732	0.0231970276	
144	1167.111	14.24903	0.041493	**144**	1167.048	5.602362	0.0255641928	
145	1227.338	1.548839	0.016728	**145**	1227.578	2.573527	0.0972407518	
146	1229.142	2.400502	0.063257	**146**	1228.625	5.915138	0.3186859367	
147	1229.838	8.662999	0.070463	**147**	1230.521	4.000353	0.1715311990	
148	1230.553	0.550808	0.080467	**148**	1231.831	0.357217	0.0454616296	
149	1231.558	1.085492	0.1435	**149**	1232.539	2.425606	0.1625926607	
150	1234.302	15.124	0.274912	**150**	1234.243	10.24886	0.1576260196	
151	1240.236	6.375389	0.013515	**151**	1240.754	7.137325	0.0269014696	
152	1241.726	8.858611	0.019692	**152**	1241.482	7.70031	0.0386964059	
153	1242.543	7.026877	0.008756	**153**	1242.391	6.858514	0.0183842360	
154	1284.639	5.186433	0.071235	**154**	1287.945	1.177046	0.1688335009	

155	1288.832	7.28895	0.121328	**155**	1289.502	6.289286	0.3132063169	
156	1293.635	6.43942	0.057402	**156**	1292.191	7.528718	0.1547241141	
157	1330.263	1.83296	0.36681	**157**	1331.87	3.001027	0.9015144130	
158	1330.667	4.384039	0.76213	**158**	1332.607	1.215134	1.0285905113	
159	1331.213	0.566997	0.941911	**159**	1333.876	0.940018	0.7161142267	
160	1347.176	0.169387	0.212968	**160**	1347.817	4.194468	0.8711687967	
161	1348.238	2.446182	0.192141	**161**	1349.308	0.41511	0.1186248838	C–N movement of phen ligand
162	1348.461	2.793695	0.252876	**162**	1349.604	1.175	0.6458464500	
163	1369.492	28.74044	0.107992	**163**	1372.254	21.80942	0.1027744452	
164	1372.831	26.02843	0.256846	**164**	1373.065	20.14361	0.5562519439	
165	1379.575	75.85224	0.187984	**165**	1378.414	48.14203	0.3030796499	
166	1432.944	4.540519	1.846455	**166**	1432.431	7.910669	2.6119246523	
167	1433.4	4.124939	2.236525	**167**	1432.775	1.974129	4.0416527017	
168	1435.061	10.71142	2.644636	**168**	1435.527	6.260081	3.1552832771	
169	1436.282	1.251025	0.228554	**169**	1437.262	3.361919	0.1168582654	
170	1437.495	8.445339	0.126887	**170**	1437.803	9.788128	0.1203703676	
171	1438.667	8.778706	0.165541	**171**	1437.992	7.899219	0.2100029607	
172	1444.091	93.47642	0.074302	**172**	1446.429	91.57533	0.1372743785	
173	1449.125	116.3782	0.06843	**173**	1448.415	127.0273	0.0537543850	
174	1454.258	115.4868	0.0242	**174**	1453.33	121.0989	0.0568029988	
175	1478.195	1.722933	0.626054	**175**	1479.754	2.243062	1.2526051078	
176	1479.949	5.759757	1.524519	**176**	1480.096	8.170188	2.2382781907	
177	1481.971	5.113365	1.444814	**177**	1481.951	4.56454	2.2491215966	
178	1531.039	10.36149	0.019714	**178**	1532.454	23.58149	0.0274042257	C–C and C–N bond

179	1532.861	20.71708	0.021935	**179**	1532.697	13.39615	0.0280994126	stretching vibrations within phenanthroline rings
180	1532.904	29.12624	0.016266	**180**	1533.373	19.03205	0.0356287703	
181	1546.956	113.0249	0.095578	**181**	1550.392	151.7013	0.2253979602	
182	1551.756	175.9568	0.204637	**182**	1552.917	197.4658	0.4732027071	
183	1556.854	125.1038	0.256145	**183**	1555.166	119.9051	0.2257791769	
184	1607.225	24.66454	0.052129	**184**	1609.947	62.38138	0.1126650537	
185	1610.859	51.44546	0.212071	**185**	1611.023	33.61916	0.3392268926	
186	1614.394	40.54182	0.174215	**186**	1613.451	39.31512	0.2093533916	
187	1630.393	17.57016	0.510327	**187**	1630.892	23.94678	1.3778508401	
188	1631.98	47.95427	0.632001	**188**	1631.133	26.25524	1.2398445798	
189	1634.71	57.00555	0.64656	**189**	1632.433	51.83889	0.6274663532	
190	1647.401	0.910291	0.194523	**190**	1647.904	0.947053	0.2857339918	
191	1648.974	4.966865	0.53124	**191**	1648.683	5.56784	0.5911366027	
192	1650.519	3.181089	0.646535	**192**	1649.191	3.356125	0.6945858784	
193	1665.273	19.56185	0.175662	**193**	1666.406	25.5185	0.4885387212	
194	1666.44	32.44373	0.398392	**194**	1667.934	28.31173	0.4552427565	
195	1670.036	23.82503	0.363547	**195**	1668.021	20.14118	0.5327519546	
196	2070.869	2618.087	1.050787	**196**	2072.794	2363.177	1.9820562789	Cyanide bond stretching
197	2079.316	2153.297	0.860805	**197**	2079.514	1714.718	2.0926683647	
198	2098.666	722.2394	1.423141	**198**	2095.448	495.8099	1.8349106498	
199	3170.553	0.260335	0.156264	**199**	3172.061	0.192297	0.1504067885	C–H bond stretching of phenanthroline rings
200	3171.423	0.075853	0.122452	**200**	3172.456	0.095822	0.1522659827	
201	3173.237	0.207564	0.161895	**201**	3172.938	0.195262	0.1744519909	
202	3177.046	9.020906	0.475221	**202**	3177.896	8.648286	0.6228980398	
203	3177.752	6.337461	0.660337	**203**	3178.885	10.7375	0.7487846630	

204	3178.051	9.049435	0.463216	**204**	3179.006	7.334504	0.6608305284	
205	3178.378	13.58618	0.83132	**205**	3180.481	8.624953	0.7316721956	
206	3178.457	6.364045	0.745106	**206**	3180.712	7.758771	0.7327134984	
207	3180.876	5.339053	0.610052	**207**	3181.253	7.284554	0.6994288949	
208	3189.897	18.86508	1.12479	**208**	3191.347	22.30582	1.3640618779	
209	3190.667	29.5225	1.894567	**209**	3191.572	31.51022	2.0715265363	
210	3191.533	32.6641	1.054431	**210**	3192.084	27.71858	2.2106365154	
211	3192.622	18.91071	1.600654	**211**	3203.641	8.992094	0.5886861505	
212	3203.528	7.111364	0.355898	**212**	3210.016	1.012258	0.4726409320	
213	3205.188	3.146025	0.689402	**213**	3211.655	4.683946	0.5776289500	
214	3208.001	5.410556	0.57139	**214**	3213.047	4.434835	0.8662072767	
215	3210.66	7.786673	0.596072	**215**	3213.201	1.915114	0.2801202484	
216	3213.011	13.74668	1.585271	**216**	3214.111	0.520192	0.1965886190	
217	3217.779	5.50483	1.155892	**217**	3216.828	11.9072	1.4507493714	
218	3217.843	0.420035	0.447758	**218**	3224.371	4.50995	0.9648406790	
219	3220.014	7.974919	1.222246	**219**	3225.843	3.704038	1.0016476142	
220	3221.632	13.37616	0.734614	**220**	3229.346	10.18429	0.8354897004	
221	3226.234	26.6903	0.735192	**221**	3230.668	2.963151	0.5549808622	
222	3231.127	1.540136	0.674748	**222**	3238.518	1.341495	0.2135558855	

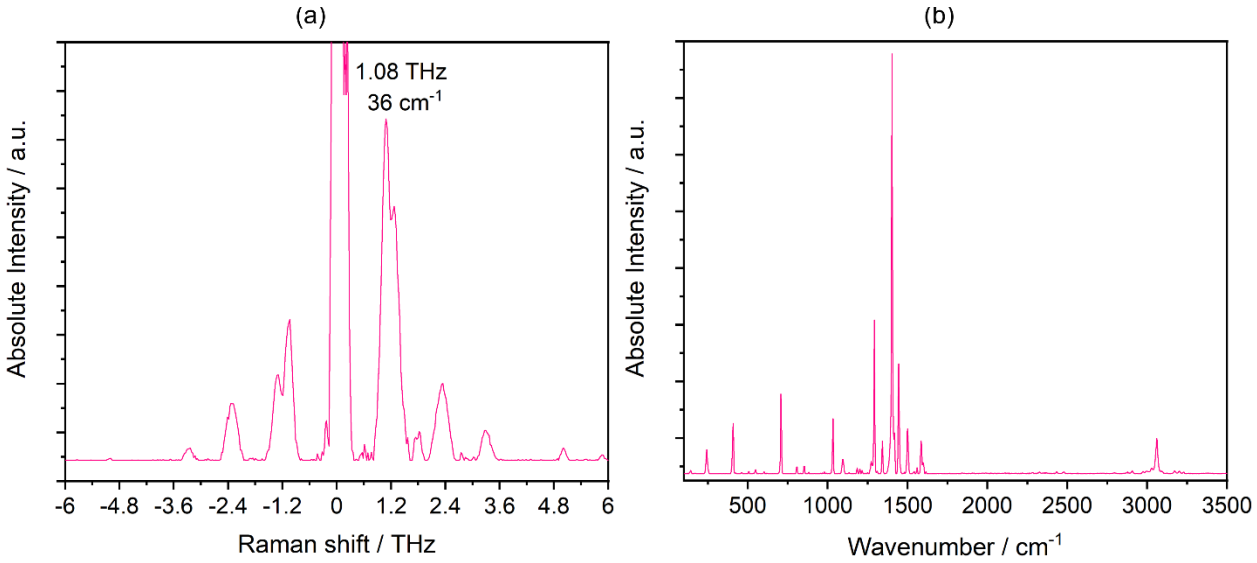


Figure S7. Experimental Raman scattering spectra for single crystals of phenanthroline in (a) the low-frequency region of -6–6 THz (-200–200 cm^{-1}) with Stokes and anti-Stokes Raman scattering signals and (b) the high-frequency region of 100–3500 cm^{-1}.

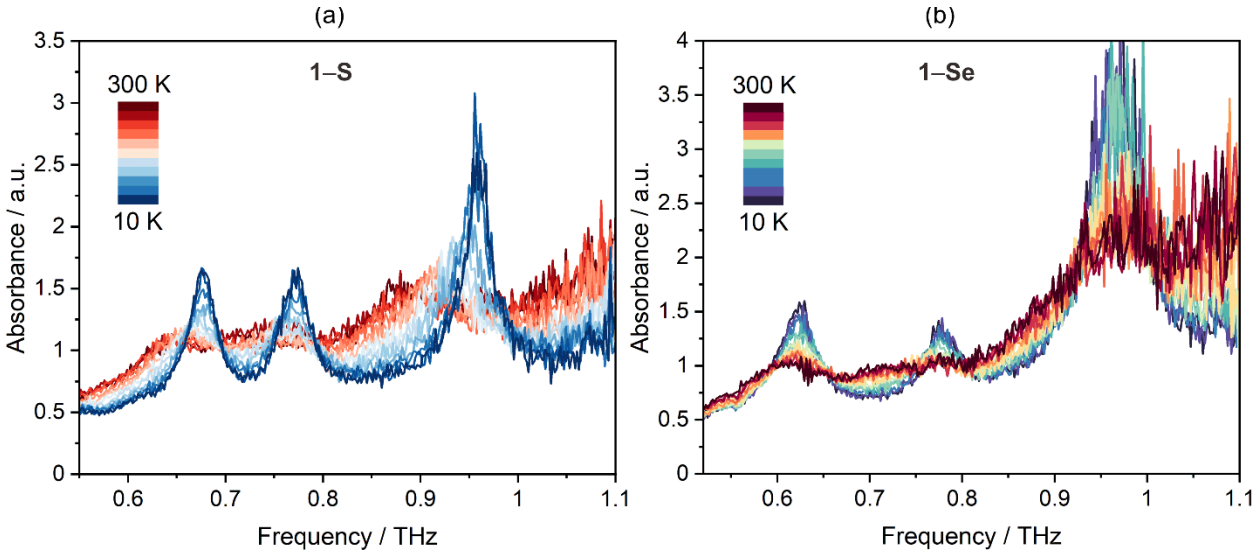


Figure S8. Temperature-dependent THz-TDS spectra of (a) **1-S** and (b) **1-Se** determined in the range of 300–10 K.

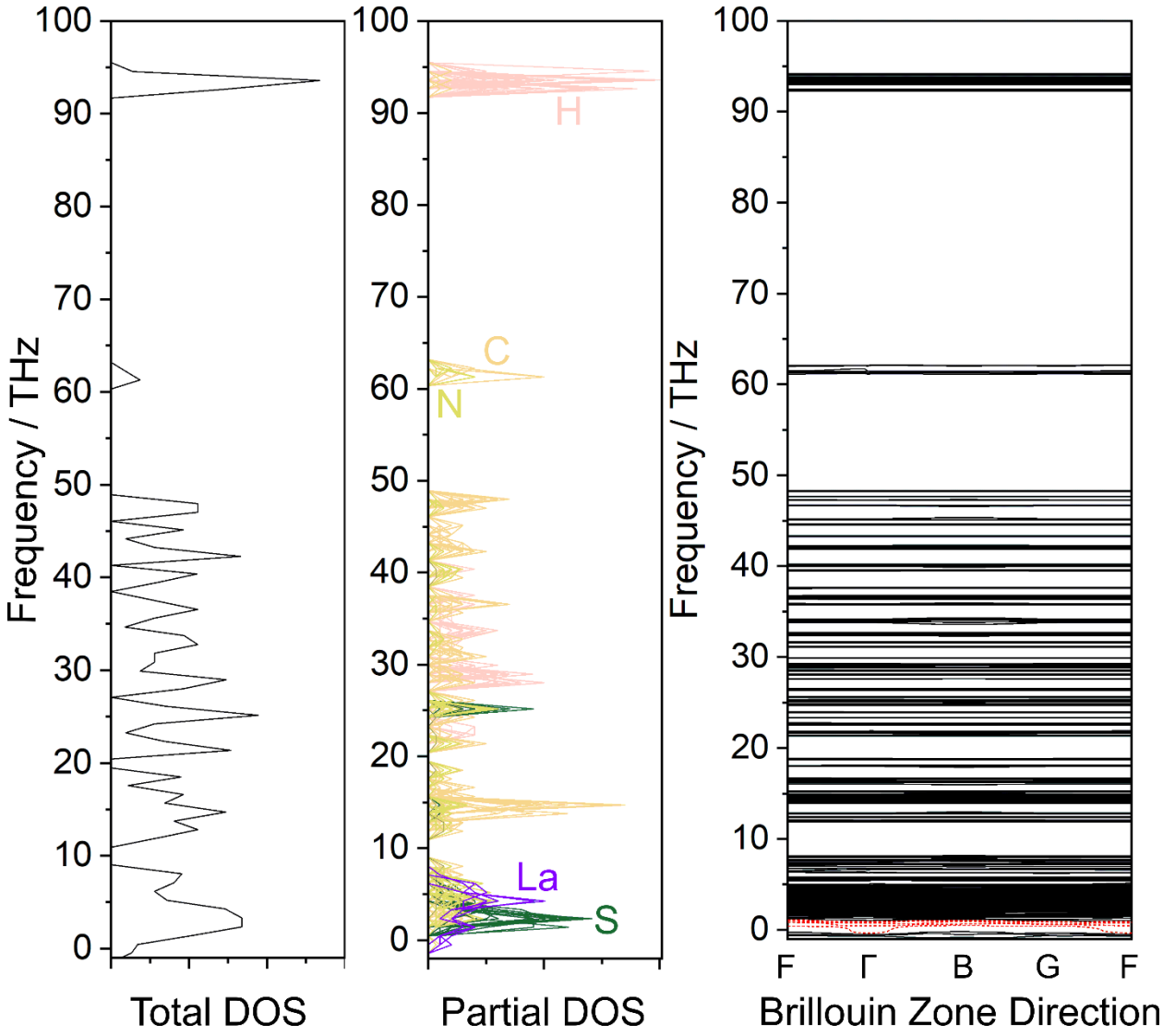


Figure S9. Total DOS of the **1-S** (black line) and partial phonon DOS of La (magenta line), S (dark green line), C (light orange line), N (light green line), and H (light pink line). The band structure of **1-S**. The dotted red-lines close to zero correspond to the vibrational band structure characterized through THz-TDS.

Table S5. Calculated optical phonon modes obtained through first-principles calculations of **1-S**.

Frequency (THz)	Frequency (cm^{-1})	IR (a.u.)	Irreducible Representation	Frequency (THz)	Frequency (cm^{-1})	IR (a.u.)	Irreducible Representation
-0.682	-22.73311	0.0000089	A(RI)	26.359	878.62455	0.0000720	A(RI)
-0.499	-16.63317	0.0000007	A(RI)	26.38	879.32454	0.0001070	A(RI)
-0.458	-15.26651	0.0002081	A(RI)	26.474	882.45784	0.0002071	A(RI)
-0.342	-11.39989	0.0000321	A(RI)	26.484	882.79117	0.0000130	A(RI)
0.445	14.83319	0.0005346	A(RI)	26.56	885.32448	0.0000039	A(RI)
0.753	25.09975	0.0001690	A(RI)	26.575	885.82448	0.0000136	A(RI)
0.844	28.13305	0.0000041	A(RI)	27.613	920.42413	0.0000696	A(RI)
0.936	31.19969	0.0000642	A(RI)	27.633	921.09079	0.0010616	A(RI)
1.071	35.69964	0.0002163	A(RI)	28.008	933.59066	0.0000069	A(RI)
1.302	43.39957	0.0000814	A(RI)	28.032	934.39066	0.0001138	A(RI)
1.453	48.43285	0.0003277	A(RI)	28.095	936.49064	0.0002707	A(RI)
1.508	50.26616	0.0001514	A(RI)	28.116	937.19063	0.0000189	A(RI)
1.564	52.13281	0.0000155	A(RI)	28.132	937.72396	0.0002543	A(RI)
1.583	52.76614	0.0011000	A(RI)	28.148	938.25728	0.0001550	A(RI)
1.676	55.86611	0.0000248	A(RI)	28.444	948.12385	0.0000000	A(RI)
1.714	57.13276	0.0000203	A(RI)	28.469	948.95718	0.0002094	A(RI)
1.808	60.26606	0.0000104	A(RI)	28.593	953.09047	0.0001762	A(RI)
1.897	63.2327	0.0000904	A(RI)	28.623	954.09046	0.0007153	A(RI)
1.992	66.39934	0.0003814	A(RI)	28.834	961.12372	0.0000462	A(RI)
2.004	66.79933	0.0001005	A(RI)	28.853	961.75705	0.0000118	A(RI)
2.077	69.23264	0.0000247	A(RI)	28.859	961.95705	0.0000100	A(RI)
2.16	71.99928	0.0002613	A(RI)	28.871	962.35704	0.0000924	A(RI)
2.23	74.33259	0.0000234	A(RI)	28.913	963.75703	0.0000208	A(RI)
2.283	76.09924	0.0003414	A(RI)	28.942	964.72369	0.0010427	A(RI)
2.309	76.9659	0.0002406	A(RI)	29.011	967.02366	0.0030085	A(RI)
2.369	78.96588	0.0000635	A(RI)	29.035	967.82366	0.0018610	A(RI)
2.438	81.26585	0.0005202	A(RI)	29.165	972.15695	0.0000555	A(RI)
2.449	81.63252	0.0000387	A(RI)	29.194	973.1236	0.0000046	A(RI)
2.472	82.39918	0.0000166	A(RI)	29.27	975.65691	0.0013443	A(RI)
2.517	83.89916	0.0007048	A(RI)	29.298	976.59023	0.0000203	A(RI)
2.585	86.16581	0.0004946	A(RI)	29.31	976.99023	0.0019104	A(RI)
2.656	88.53245	0.0002751	A(RI)	29.322	977.39023	0.0005182	A(RI)
2.695	89.83244	0.0000112	A(RI)	29.91	996.99003	0.0006134	A(RI)
2.753	91.76575	0.0000170	A(RI)	29.919	997.29003	0.0010469	A(RI)
2.781	92.69907	0.0003807	A(RI)	29.93	997.65669	0.0007933	A(RI)
2.825	94.16573	0.0000094	A(RI)	29.938	997.92335	0.0002648	A(RI)
2.899	96.63237	0.0004937	A(RI)	31.083	1036.08964	0.0000014	A(RI)
2.957	98.56568	0.0002065	A(RI)	31.108	1036.92296	0.0000425	A(RI)
3.013	100.43233	0.0002026	A(RI)	31.157	1038.55628	0.0000449	A(RI)
3.11	103.66563	0.0000474	A(RI)	31.163	1038.75628	0.0004187	A(RI)
3.118	103.93229	0.0002323	A(RI)	31.179	1039.28961	0.0021223	A(RI)
3.207	106.89893	0.0000097	A(RI)	31.242	1041.38959	0.0008567	A(RI)
3.217	107.23226	0.0003035	A(RI)	31.561	1052.02281	0.0000009	A(RI)

3.277	109.23224	0.0000556	A(RI)	31.568	1052.25614	0.0000028	A(RI)
3.287	109.56557	0.0010500	A(RI)	31.583	1052.75614	0.0000004	A(RI)
3.369	112.29888	0.0004986	A(RI)	31.602	1053.38947	0.0001106	A(RI)
3.423	114.09886	0.0006635	A(RI)	31.673	1055.75611	0.0003885	A(RI)
3.453	115.09885	0.0004027	A(RI)	31.725	1057.48943	0.0001499	A(RI)
3.488	116.2655	0.0001644	A(RI)	32.351	1078.35588	0.0018242	A(RI)
3.57	118.99881	0.0056500	A(RI)	32.387	1079.55587	0.0000382	A(RI)
3.643	121.43212	0.0000660	A(RI)	32.406	1080.1892	0.0003140	A(RI)
3.688	122.9321	0.0002536	A(RI)	32.413	1080.42253	0.0052762	A(RI)
3.731	124.36542	0.0003509	A(RI)	32.44	1081.32252	0.0029272	A(RI)
3.819	127.29873	0.0002858	A(RI)	32.449	1081.62252	0.0000194	A(RI)
3.862	128.73205	0.0004908	A(RI)	32.581	1086.02247	0.0026154	A(RI)
3.894	129.7987	0.0001076	A(RI)	32.609	1086.9558	0.0004614	A(RI)
3.895	129.83204	0.0000117	A(RI)	32.636	1087.85579	0.0014094	A(RI)
3.934	131.13202	0.0047700	A(RI)	32.661	1088.68911	0.0005365	A(RI)
4.019	133.96533	0.0004516	A(RI)	32.716	1090.52243	0.0004416	A(RI)
4.104	136.79863	0.0040600	A(RI)	32.739	1091.28909	0.0001967	A(RI)
4.152	138.39862	0.0008143	A(RI)	33.82	1127.32206	0.0002331	A(RI)
4.206	140.1986	0.0000647	A(RI)	33.836	1127.85539	0.0000153	A(RI)
4.292	143.06524	0.0007940	A(RI)	33.884	1129.45537	0.0097434	A(RI)
4.344	144.79855	0.0000568	A(RI)	33.893	1129.75537	0.0008351	A(RI)
4.432	147.73186	0.0003050	A(RI)	34.018	1133.92199	0.0187191	A(RI)
4.462	148.73185	0.0058000	A(RI)	34.03	1134.32199	0.0000779	A(RI)
4.572	152.39848	0.0007843	A(RI)	34.078	1135.92197	0.0008408	A(RI)
4.616	153.86513	0.0000121	A(RI)	34.106	1136.8553	0.0028335	A(RI)
4.7	156.6651	0.0023700	A(RI)	34.133	1137.75529	0.0029058	A(RI)
4.766	158.86508	0.0031700	A(RI)	34.194	1139.7886	0.0020129	A(RI)
4.884	162.79837	0.0045800	A(RI)	34.203	1140.0886	0.0001866	A(RI)
4.902	163.39837	0.0069800	A(RI)	34.213	1140.42193	0.0003600	A(RI)
4.943	164.76502	0.0078900	A(RI)	35.757	1191.88808	0.0040026	A(RI)
5.071	169.03164	0.0020400	A(RI)	35.79	1192.98807	0.0000717	A(RI)
5.439	181.29819	0.0013800	A(RI)	35.841	1194.68805	0.0000000	A(RI)
5.514	183.79816	0.0018400	A(RI)	35.86	1195.32138	0.0000316	A(RI)
5.585	186.16481	0.0193600	A(RI)	35.888	1196.2547	0.0000029	A(RI)
5.649	188.29812	0.0018000	A(RI)	35.901	1196.68803	0.0000005	A(RI)
5.751	191.69808	0.0017900	A(RI)	36.38	1212.65454	0.0000490	A(RI)
5.858	195.26471	0.0000752	A(RI)	36.404	1213.45453	0.0001675	A(RI)
6.259	208.63125	0.0774400	A(RI)	36.494	1216.4545	0.0000459	A(RI)
6.312	210.3979	0.0305600	A(RI)	36.524	1217.45449	0.0005833	A(RI)
6.678	222.59777	0.0008061	A(RI)	36.553	1218.42115	0.0000764	A(RI)
6.713	223.76443	0.0017200	A(RI)	36.559	1218.62115	0.0000582	A(RI)
6.84	227.99772	0.0068300	A(RI)	36.659	1221.95445	0.0002031	A(RI)
6.997	233.231	0.0001218	A(RI)	36.736	1224.52109	0.0000781	A(RI)
7.198	239.93093	0.0001245	A(RI)	36.744	1224.78775	0.0004593	A(RI)
7.281	242.69757	0.0033500	A(RI)	36.76	1225.32108	0.0002580	A(RI)
7.284	242.79757	0.0001663	A(RI)	36.781	1226.02107	0.0000962	A(RI)
7.323	244.09756	0.0010100	A(RI)	36.802	1226.72107	0.0022409	A(RI)

7.417	247.23086	0.0005295	A(RI)	37.565	1252.15415	0.0008427	A(RI)
7.562	252.06415	0.0000554	A(RI)	37.591	1253.0208	0.0000202	A(RI)
7.607	253.56413	0.0002124	A(RI)	37.614	1253.78746	0.0098188	A(RI)
7.613	253.76413	0.0000933	A(RI)	37.673	1255.75411	0.0000636	A(RI)
7.669	255.63078	0.0006787	A(RI)	37.684	1256.12077	0.0001129	A(RI)
7.734	257.79742	0.0006567	A(RI)	37.71	1256.98743	0.0001954	A(RI)
7.975	265.83068	0.0005211	A(RI)	39.475	1315.82018	0.0011049	A(RI)
8.015	267.164	0.0005811	A(RI)	39.491	1316.3535	0.0000359	A(RI)
8.04	267.99732	0.0001641	A(RI)	39.504	1316.78683	0.0000487	A(RI)
8.064	268.79731	0.0010500	A(RI)	39.521	1317.35349	0.0000220	A(RI)
8.119	270.63063	0.0011500	A(RI)	39.608	1320.25346	0.0000627	A(RI)
8.144	271.46395	0.0003332	A(RI)	39.628	1320.92012	0.0000813	A(RI)
11.883	396.09604	0.0000006	A(RI)	39.973	1332.42001	0.0006072	A(RI)
11.957	398.56268	0.0000001	A(RI)	40.004	1333.45333	0.0000446	A(RI)
11.987	399.56267	0.0000820	A(RI)	40.026	1334.18666	0.0003291	A(RI)
12.016	400.52933	0.0000078	A(RI)	40.041	1334.68665	0.0000656	A(RI)
12.077	402.56264	0.0001077	A(RI)	40.059	1335.28665	0.0005078	A(RI)
12.097	403.2293	0.0000350	A(RI)	40.083	1336.08664	0.0000771	A(RI)
12.369	412.29588	0.0002427	A(RI)	40.096	1336.51997	0.0008284	A(RI)
12.386	412.86254	0.0004801	A(RI)	40.117	1337.21996	0.0013387	A(RI)
12.418	413.92919	0.0007795	A(RI)	40.204	1340.11993	0.0007624	A(RI)
12.429	414.29586	0.0000323	A(RI)	40.23	1340.98659	0.0001182	A(RI)
12.464	415.46251	0.0003891	A(RI)	40.239	1341.28659	0.0003677	A(RI)
12.501	416.69583	0.0007649	A(RI)	40.282	1342.71991	0.0000300	A(RI)
12.748	424.92908	0.0000714	A(RI)	41.884	1396.11937	0.0001286	A(RI)
12.77	425.66241	0.0001640	A(RI)	41.9	1396.6527	0.0005336	A(RI)
12.8	426.6624	0.0000015	A(RI)	41.914	1397.11936	0.0001134	A(RI)
12.821	427.36239	0.0000970	A(RI)	41.921	1397.35269	0.0000532	A(RI)
12.843	428.09572	0.0000177	A(RI)	42	1399.986	0.0000731	A(RI)
12.893	429.76237	0.0004750	A(RI)	42.014	1400.45266	0.0006492	A(RI)
13.942	464.72869	0.0000148	A(RI)	42.016	1400.51933	0.0025249	A(RI)
13.96	465.32868	0.0000168	A(RI)	42.034	1401.11932	0.0062694	A(RI)
13.988	466.262	0.0000010	A(RI)	42.055	1401.81932	0.0094127	A(RI)
13.998	466.59533	0.0000008	A(RI)	42.057	1401.88598	0.0005171	A(RI)
14.081	469.36197	0.0000219	A(RI)	42.059	1401.95265	0.0018691	A(RI)
14.087	469.56197	0.0000183	A(RI)	42.07	1402.31931	0.0001440	A(RI)
14.191	473.0286	0.0007761	A(RI)	42.173	1405.75261	0.0161648	A(RI)
14.218	473.92859	0.0004721	A(RI)	42.191	1406.3526	0.0022162	A(RI)
14.259	475.29525	0.0009011	A(RI)	42.217	1407.21926	0.0119535	A(RI)
14.303	476.7619	0.0015500	A(RI)	42.282	1409.38591	0.0000189	A(RI)
14.334	477.79522	0.0006202	A(RI)	42.307	1410.21923	0.0000892	A(RI)
14.362	478.72855	0.0000762	A(RI)	42.311	1410.35256	0.0000728	A(RI)
14.458	481.92851	0.0001927	A(RI)	43.278	1442.58557	0.0001962	A(RI)
14.495	483.16184	0.0000694	A(RI)	43.288	1442.9189	0.0000210	A(RI)
14.51	483.66183	0.0005624	A(RI)	43.307	1443.55223	0.0000664	A(RI)
14.555	485.16182	0.0000030	A(RI)	43.309	1443.6189	0.0001937	A(RI)
14.671	489.02844	0.0000297	A(RI)	43.36	1445.31888	0.0000025	A(RI)

14.746	491.52842	0.0000005	A(RI)	43.38	1445.98554	0.0005272	A(RI)
14.789	492.96174	0.0001047	A(RI)	44.581	1486.01847	0.0002790	A(RI)
14.812	493.7284	0.0000221	A(RI)	44.606	1486.8518	0.0001876	A(RI)
14.834	494.46172	0.0000080	A(RI)	44.674	1489.11844	0.0056176	A(RI)
14.868	495.59504	0.0000003	A(RI)	44.684	1489.45177	0.0000055	A(RI)
14.936	497.86169	0.0000029	A(RI)	44.691	1489.6851	0.0024974	A(RI)
14.947	498.22835	0.0000908	A(RI)	44.707	1490.21843	0.0013565	A(RI)
15.207	506.89493	0.0000557	A(RI)	45.115	1503.8183	0.0038967	A(RI)
15.212	507.0616	0.0000000	A(RI)	45.135	1504.48496	0.0001800	A(RI)
15.219	507.29493	0.0000018	A(RI)	45.14	1504.65162	0.0000414	A(RI)
15.232	507.72826	0.0000079	A(RI)	45.159	1505.28495	0.0180496	A(RI)
15.291	509.6949	0.0003560	A(RI)	45.199	1506.61827	0.0013976	A(RI)
15.335	511.16156	0.0002954	A(RI)	45.238	1507.91825	0.0047727	A(RI)
16.05	534.99465	0.0000014	A(RI)	46.653	1555.08445	0.0104852	A(RI)
16.072	535.72798	0.0000000	A(RI)	46.665	1555.48445	0.0086546	A(RI)
16.243	541.42792	0.0000000	A(RI)	46.69	1556.31777	0.0044134	A(RI)
16.268	542.26124	0.0000001	A(RI)	46.713	1557.08443	0.0004620	A(RI)
16.327	544.22789	0.0000000	A(RI)	46.716	1557.18443	0.0001720	A(RI)
16.36	545.32788	0.0000373	A(RI)	46.752	1558.38442	0.0002344	A(RI)
16.499	549.96117	0.0000184	A(RI)	47.246	1574.85092	0.0011005	A(RI)
16.542	551.39449	0.0000177	A(RI)	47.249	1574.95092	0.0000020	A(RI)
16.57	552.32781	0.0000039	A(RI)	47.292	1576.38424	0.0000672	A(RI)
16.598	553.26113	0.0000204	A(RI)	47.309	1576.9509	0.0001267	A(RI)
16.665	555.49445	0.0002486	A(RI)	47.317	1577.21756	0.0015060	A(RI)
16.722	557.39443	0.0002040	A(RI)	47.318	1577.25089	0.0008565	A(RI)
17.999	599.96067	0.0002952	A(RI)	47.691	1589.6841	0.0001888	A(RI)
18.014	600.46066	0.0002536	A(RI)	47.702	1590.05077	0.0001775	A(RI)
18.082	602.72731	0.0000511	A(RI)	47.708	1590.25076	0.0000213	A(RI)
18.098	603.26063	0.0003165	A(RI)	47.721	1590.68409	0.0000522	A(RI)
18.104	603.46063	0.0000471	A(RI)	47.736	1591.18409	0.0000468	A(RI)
18.132	604.39396	0.0000021	A(RI)	47.742	1591.38409	0.0000661	A(RI)
18.736	624.52709	0.0005293	A(RI)	48.219	1607.28393	0.0004975	A(RI)
18.772	625.72708	0.0001645	A(RI)	48.241	1608.01725	0.0021081	A(RI)
18.784	626.12707	0.0027300	A(RI)	48.263	1608.75058	0.0005125	A(RI)
18.796	626.52707	0.0001748	A(RI)	48.293	1609.75057	0.0003536	A(RI)
18.84	627.99372	0.0001304	A(RI)	48.313	1610.41723	0.0006118	A(RI)
18.88	629.32704	0.0001441	A(RI)	48.337	1611.21722	0.0018731	A(RI)
21.32	710.65956	0.0032000	A(RI)	61.148	2038.24628	0.8031403	A(RI)
21.326	710.85956	0.0000910	A(RI)	61.293	2043.07957	0.1308098	A(RI)
21.351	711.69288	0.0032300	A(RI)	61.445	2048.14619	0.0030711	A(RI)
21.361	712.02621	0.0028200	A(RI)	61.555	2051.81282	0.8045058	A(RI)
21.382	712.72621	0.0001387	A(RI)	62.119	2070.61263	0.0728309	A(RI)
21.406	713.5262	0.0008240	A(RI)	62.139	2071.27929	0.0747707	A(RI)
21.627	720.89279	0.0006997	A(RI)	92.29	3076.30257	0.0002769	A(RI)
21.641	721.35945	0.0071400	A(RI)	92.29	3076.30257	0.0083962	A(RI)
21.649	721.62612	0.0096200	A(RI)	92.353	3078.40255	0.0057605	A(RI)
21.656	721.85945	0.0000542	A(RI)	92.368	3078.90254	0.0006011	A(RI)

21.676	722.52611	0.0014700	A(RI)	92.472	3082.36918	0.0006487	A(RI)
21.694	723.1261	0.0025900	A(RI)	92.506	3083.5025	0.0005680	A(RI)
21.734	724.45942	0.0546000	A(RI)	93.005	3100.13567	0.0000137	A(RI)
21.775	725.82608	0.0002760	A(RI)	93.013	3100.40233	0.0002154	A(RI)
21.779	725.95941	0.0000007	A(RI)	93.023	3100.73566	0.0001005	A(RI)
21.827	727.55939	0.0000106	A(RI)	93.041	3101.33565	0.0013433	A(RI)
21.872	729.05938	0.0012700	A(RI)	93.042	3101.36899	0.0057779	A(RI)
21.89	729.65937	0.0028700	A(RI)	93.044	3101.43565	0.0035257	A(RI)
22.562	752.05915	0.0086100	A(RI)	93.069	3102.26898	0.0000085	A(RI)
22.612	753.7258	0.0000000	A(RI)	93.078	3102.56897	0.0014856	A(RI)
22.642	754.72579	0.0014800	A(RI)	93.08	3102.63564	0.0000085	A(RI)
22.652	755.05912	0.0002956	A(RI)	93.093	3103.06897	0.0006505	A(RI)
22.7	756.6591	0.0000000	A(RI)	93.152	3105.03562	0.0007551	A(RI)
22.78	759.32574	0.0053000	A(RI)	93.171	3105.66894	0.0008619	A(RI)
23.31	776.99223	0.0001560	A(RI)	93.225	3107.46893	0.0001795	A(RI)
23.339	777.95889	0.0000071	A(RI)	93.228	3107.56892	0.0002720	A(RI)
23.903	796.7587	0.0002486	A(RI)	93.294	3109.7689	0.0003269	A(RI)
23.972	799.05868	0.0008496	A(RI)	93.305	3110.13557	0.0011361	A(RI)
23.975	799.15868	0.0092700	A(RI)	93.357	3111.86888	0.0000090	A(RI)
24.007	800.22533	0.0003687	A(RI)	93.359	3111.93555	0.0030033	A(RI)
24.692	823.05844	0.0001308	A(RI)	93.362	3112.03555	0.0022326	A(RI)
24.705	823.49177	0.0003208	A(RI)	93.379	3112.60221	0.0011609	A(RI)
24.71	823.65843	0.0000008	A(RI)	93.411	3113.66886	0.0069178	A(RI)
24.743	824.75842	0.0000013	A(RI)	93.436	3114.50219	0.0042866	A(RI)
24.754	825.12508	0.0000759	A(RI)	93.509	3116.9355	0.0000000	A(RI)
24.765	825.49175	0.0016800	A(RI)	93.525	3117.46883	0.0000477	A(RI)
24.853	828.42505	0.0000007	A(RI)	93.54	3117.96882	0.0002654	A(RI)
24.878	829.25837	0.0000140	A(RI)	93.549	3118.26882	0.0002912	A(RI)
24.904	830.12503	0.0002236	A(RI)	93.572	3119.03548	0.0002968	A(RI)
24.928	830.92502	0.0000018	A(RI)	93.6	3119.9688	0.0003384	A(RI)
25.081	836.02497	0.0254800	A(RI)	93.626	3120.83546	0.0000015	A(RI)
25.087	836.22497	0.0002729	A(RI)	93.667	3122.20211	0.0001832	A(RI)
25.137	837.89162	0.0114500	A(RI)	93.717	3123.86876	0.0026272	A(RI)
25.151	838.35828	0.0054400	A(RI)	93.722	3124.03543	0.0068844	A(RI)
25.232	841.05826	0.0340100	A(RI)	93.743	3124.73542	0.0000328	A(RI)
25.256	841.85825	0.0001038	A(RI)	93.747	3124.86875	0.0087413	A(RI)
25.312	843.7249	0.0048400	A(RI)	93.858	3128.56871	0.0030143	A(RI)
25.369	845.62488	0.0022800	A(RI)	93.868	3128.90204	0.0025221	A(RI)
25.595	853.15814	0.0004503	A(RI)	94.057	3135.20198	0.0000129	A(RI)
25.623	854.09146	0.0002490	A(RI)	94.063	3135.40198	0.0000054	A(RI)
25.637	854.55812	0.0000883	A(RI)	94.075	3135.80198	0.0000145	A(RI)
25.646	854.85812	0.0002289	A(RI)	94.09	3136.30197	0.0000042	A(RI)
25.662	855.39145	0.0011800	A(RI)	94.222	3140.70193	0.0000223	A(RI)
25.687	856.22477	0.0027300	A(RI)	94.239	3141.26859	0.0000094	A(RI)

A(RI) - 1, x, y, z, x^2, y^2, z^2, xy, xz, yz (symmetry operation); (RI) - Raman and infrared active mode

UV-VIS spectroscopy

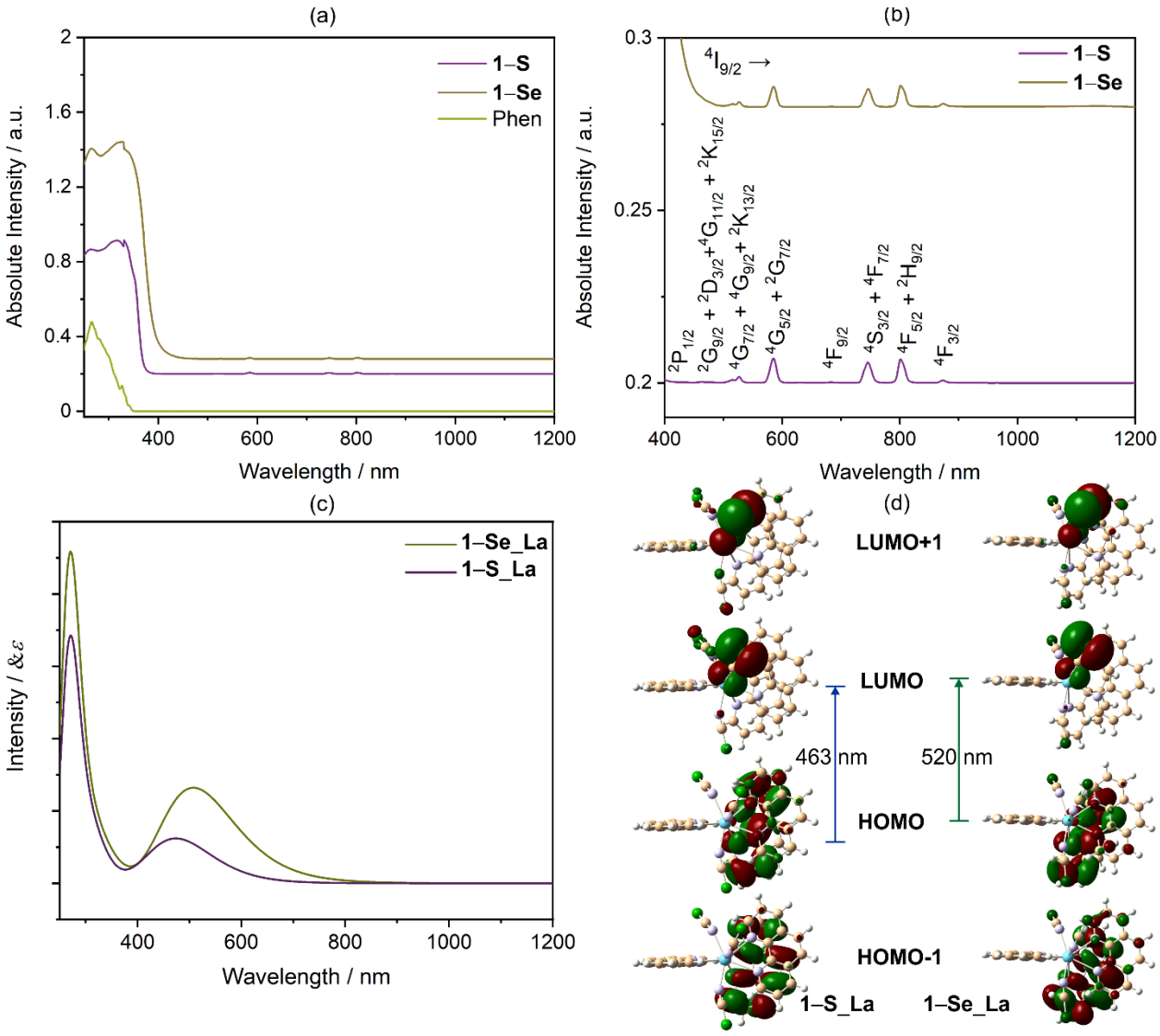


Figure S10. Room-temperature solid-state UV-Vis-NIR absorption (Kubelka-Munk function) spectra of **1-S** and **1-Se** in (a) 200–1200 nm and (b) 400–1200 nm ranges with indicated assignments, (c) the calculated UV-Vis spectra for **1-S** and **1-Se** with Nd(III) substituted by La(III) in 200–1200 nm range, and (d) obtained corresponding frontier molecular orbitals.

Emission spectroscopy and thermometric properties

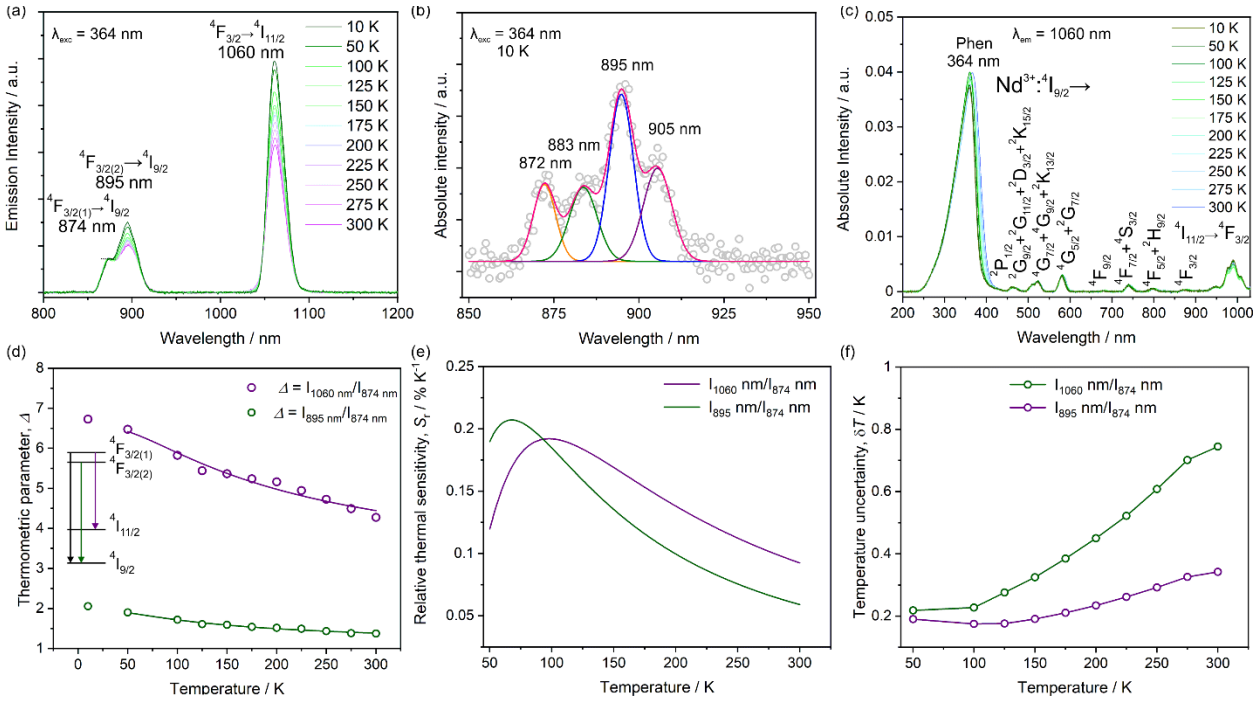


Figure S11. (a) Temperature-dependent emission spectra of **1-Se**. (b) Deconvoluted high-resolution emission spectrum measured at 10 K for **1-Se** with a 364 nm excitation light. (c) Temperature-dependent excitation spectra of **1-Se** were measured for emissive peaks located at 1060 nm. The full characterization of NIR based emissive thermometry for **1-Se** with the Δ being defined as the ratio between peak intensities, evaluated from emission intensities measured at a different temperature: (d) thermometric parameters in the 10–300 K range (magenta and olive circles) along with the fitted line in the range of 50–300 K, (e) the evaluated relative sensitivity at a different temperature from the fitted Δ curve, (f) evaluated temperature uncertainty for different temperatures.

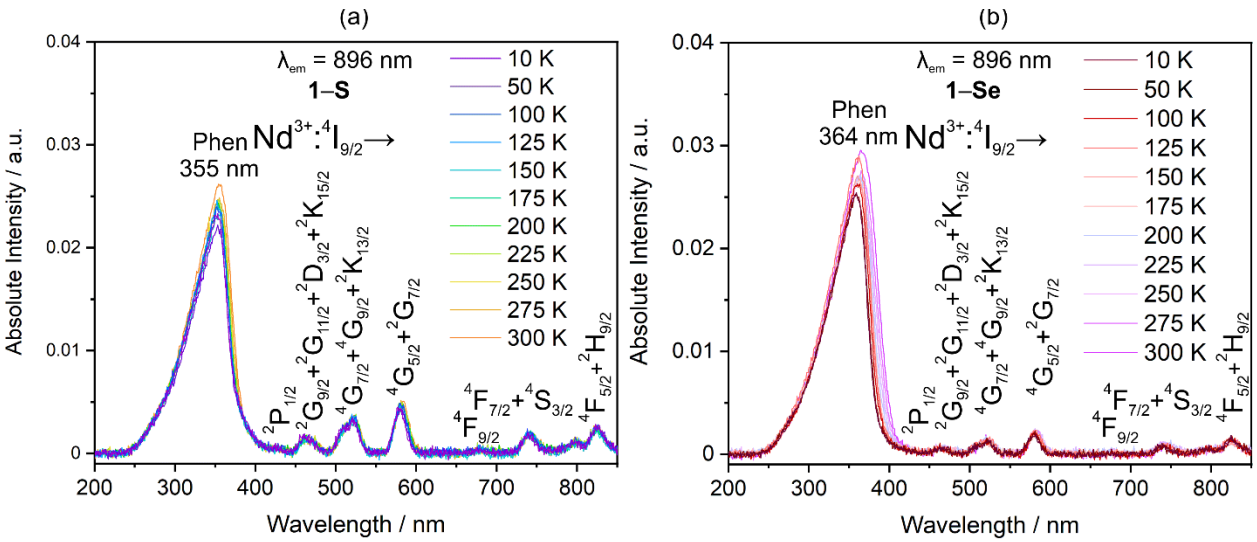


Figure S12. (a, b) Temperature-dependent excitation spectra of **1-S** and**1-Se** recorded for emissive peak centered at 896 nm.

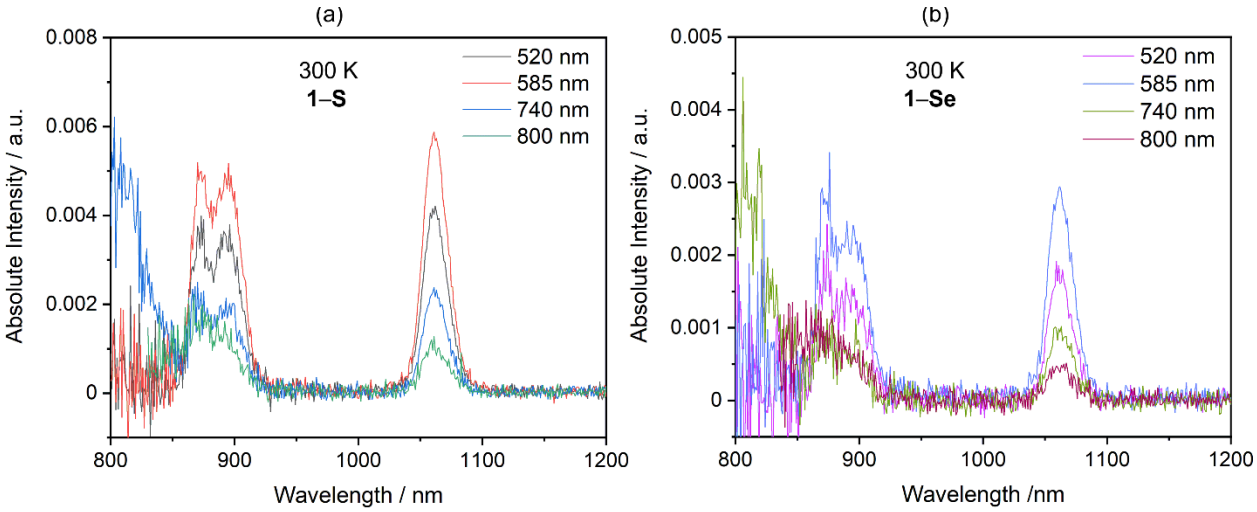


Figure S13. (a, b) Excitation wavelength-dependent near-infrared emission spectra collected at 300 K for **1-S** and **1-Se**.

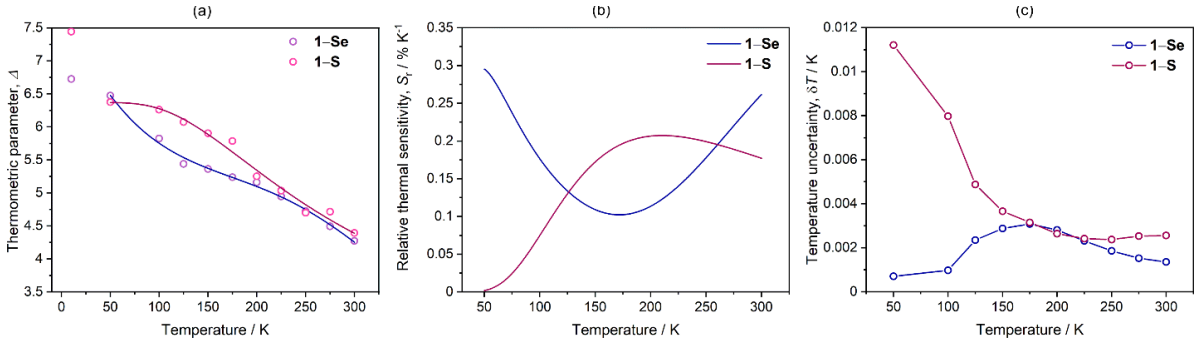


Figure S14. (a) Thermometric parameters measured in the 10–300 K range along with the fitted line in the range of 50–300 K for peaks positioned near 1060 nm and 874 nm. (b) Evaluated relative sensitivity at a different temperature from the fitted Δ curve. (c) Evaluated temperature uncertainty for different temperatures. Equation S1 was used to fit panel (a).

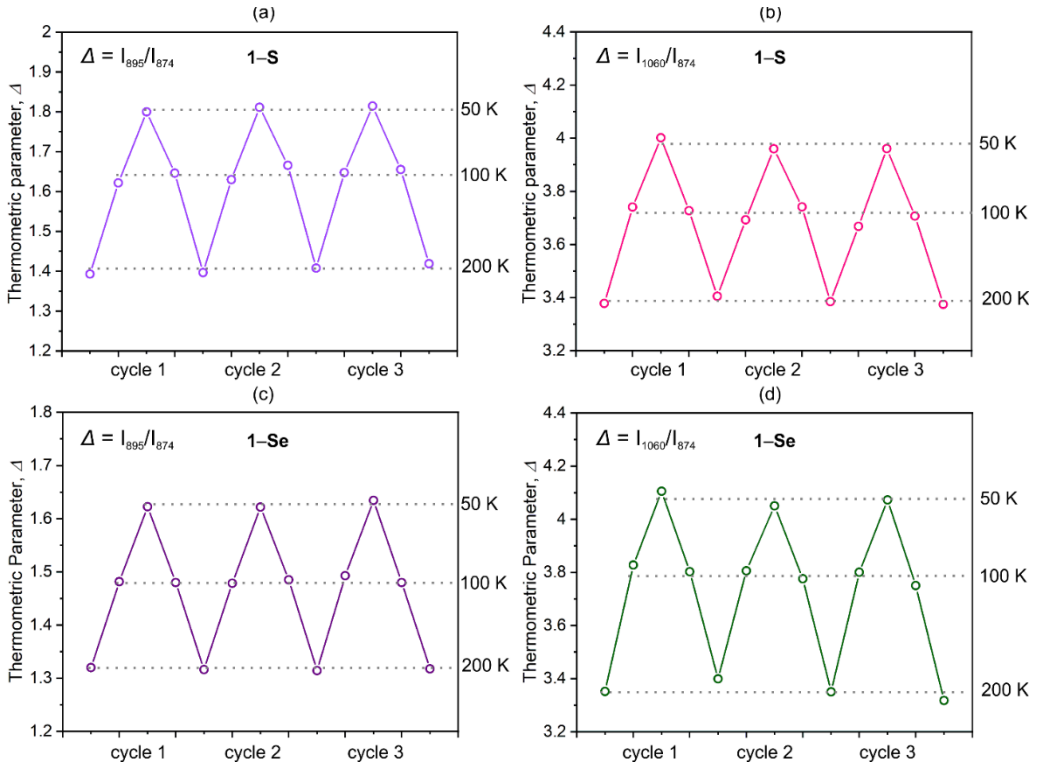


Figure S15. Three cycles of repeatability data of thermometric parameters measured for three temperatures 50, 100, and 200 K for indicated thermometric parameters.

Table S6: CASSCF–SO results for the $^4F_{9/2}$ ground term of **1-S**.

Energy (cm^{-1})	$g_\perp$	$g_\parallel$	CF wave function composition	$\langle \hat{J}_z \rangle$
0.0	1.88	4.32	16.0 % |±1/2⟩ + 3.4 % |∓3/2⟩ + 8.4 % |±5/2⟩+19.1 % |±7/2⟩ + 49.7 % |±9/2⟩	±2.162
66.5	1.07	2.82	26.1 % |±1/2⟩ + 28.6 % |∓3/2⟩ + 24.3 % |±5/2⟩+6.7 % |±7/2⟩ + 13.7 % |±9/2⟩	±0.518
122.4	1.23	3.57	7.2 % |±1/2⟩ + 20.0 % |∓3/2⟩ + 16.5 % |±5/2⟩+44.1 % |±7/2⟩ + 12.3 % |±9/2⟩	±1.571
154.2	1.94	3.63	33.5 % |±1/2⟩ + 27.5 % |∓3/2⟩ + 20.3 % |±5/2⟩+6.1 % |±7/2⟩ + 12.6 % |±9/2⟩	±1.042
210.3	1.96	4.55	16.9 % |±1/2⟩ + 16.8 % |∓3/2⟩ + 29.3 % |±5/2⟩+19.0 % |±7/2⟩ + 18.0 % |±9/2⟩	±1.376

Table S7: CASSCF–SO results for the $^4F_{9/2}$ ground term of **1-Se**.

Energy (cm^{-1})	$g_\perp$	$g_\parallel$	CF wave function composition	$\langle \hat{J}_z \rangle$
0.0	1.71	4.46	16.0 % |±1/2⟩ + 6.8 % |∓3/2⟩ + 9.5 % |±5/2⟩+17.2 % |±7/2⟩ + 5.9 % |±9/2⟩	±2.232
68.9	1.09	2.78	23.9 % |±1/2⟩ + 29.6 % |∓3/2⟩ + 26.2 % |±5/2⟩+7.2 % |±7/2⟩ + 13.0 % |±9/2⟩	±0.508
125.4	1.28	3.53	5.1 % |±1/2⟩ + 21.5 % |∓3/2⟩ + 19.8 % |±5/2⟩+43.0 % |±7/2⟩ + 10.4 % |±9/2⟩	±1.512
159.0	1.78	3.83	36.9 % |±1/2⟩ + 27.3 % |∓3/2⟩ + 17.7 % |±5/2⟩+6.9 % |±7/2⟩ + 11.2 % |±9/2⟩	±0.934
213.0	1.88	4.62	18.1 % |±1/2⟩ + 14.7 % |∓3/2⟩ + 27.8 % |±5/2⟩+23.7 % |±7/2⟩ + 15.6 % |±9/2⟩	±1.349

Mott–Seitz model for two electronic transitions[2]

$$\Delta(T) = \frac{\Delta_{10}}{[1+\alpha_1 \exp\left(-\frac{\Delta E_1}{k_B T}\right)+\alpha_2 \exp\left(-\frac{\Delta E_2}{k_B T}\right)]} \quad \textbf{(S1)}$$

where Δ_{10} is the thermometric parameter at T = 0 K, α_1 and α_2 is the ratio between nonradiative (W_0 at T = 0 K) and radiative (W_R) rates are W_0/W_R for 1060 and 874 nm, respectively, and ΔE_1, ΔE_2 is the activation energies of the nonradiative channels for 1060 and 874 nm transition.

Table S8. List of the fitting parameters from Δ vs. temperature plot for **1-S** and **1-Se** fitted with Equation 1 given in the manuscript and Equation S1.

Compounds	parameter	Δ(895/874)	Δ(1060/874)	Δ(1060/874)_mott Seitz model
1-S	A	2.131	6.402	
	Δ_0	-2.091	-7.740	
	$\Delta E_0/k_B$	374.529	400.361	
	Δ_{10}			6.368
	$\Delta E_1/k_B$			512.698
	α_1			1.992
	$\Delta E_2/k_B$			512.665
	α_2			0.500
	$R^2(COD)$	0.987	0.983	0.991
1-Se	A	1.967	6.525	
	Δ_0	-0.887	-3.761	
	$\Delta E_0/k_B$	126.118	177.695	
	Δ_{10}			7.001
	$\Delta E_1/k_B$			1527.857
	α_1			36.868
	$\Delta E_2/k_B$			98.964
	α_2			0.584
	$R^2(COD)$	0.984	0.965	0.991

Table S9. The summary of maximum and minimum calculated relative thermal sensitivity, S_r, and temperature uncertainty, ΔT, for **1-S** and **1-Se** at the indicated temperature.

Compound	parameters	Δ(895/874)	Δ(1060/874)	Δ(1060/874)_mott Seitz model
1-S	S_r (max., % K^{-1})	0.168@230 K	0.207@300 K	0.207@200 K
	S_r (min., % K^{-1})	0.006@50 K	0.008@50 K	0.003@50 K
	ΔT (max., K)	1.148@50 K	1.151@50 K	0.011@50 K
	ΔT (min., K)	0.319@250 K	0.344@250 K	0.002@250 K
1-Se	S_r (max., % K^{-1})	0.207@170 K	0.192@100 K	0.295@50 K
	S_r (min., % K^{-1})	0.0509@300 K	0.092@300 K	0.102@170 K
	ΔT (max., K)	0.341@300 K	0.744@300 K	0.003@175 K
	ΔT (min., K)	0.227@100 K	0.175@100 K	0.0008@50 K

References to Supporting Information

(1) M. Llunell, D. Casanova, J. Cirera, J. Bofill, P. Alemany, S. Alvarez, M. Pinsky and D. Avnir, *SHAPE v.2.1.* Program for the Calculation of Continuous Shape Measures of Polygonal and Polyhedral Molecular Fragments, University of Barcelona: Barcelona, Spain, 2013.

(2) Kumar, K.; Chorazy, S.; Nakabayashi, K.; Sato, H.; Sieklucka, B.; Ohkoshi, S.I. TbCo and Tb 0.5 Dy 0.5 Co layered cyanido-bridged frameworks for construction of colorimetric and ratiometric luminescent thermometers. *J. Mater. Chem. C* **2018**, *6*, 8372–8384