Supporting Information

Synthesis, optical, electronic and magnetic studies of air-stable chiral Cu(II) chlorides

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1. Materials and methods

Starting materials

All starting materials for synthesis were purchased commercially and were used without further purification. Copper (II) Chloride anhydrous, 98% was purchased from thermo scientific, Hydrochloric acid ACS reagent was purchased from Fischer Chemical and (s)-4,5,6,7-Tetrahydrobenzo[d]thiazole-2,6-diamine and (r)- 4,5,6,7-Tetrahydrobenzo[d]thiazole-2,6-diamine (THBTD) were purchased from AstaTech.

XRD measurements

Single-crystal X-ray diffraction

X-ray diffraction data were measured on a Bruker D8 Venture Photon II diffractometer equipped with a Cu Kα INCOATEC ImuS micro-focus source ($\lambda = 1.54178$ Å) and Bruker SMART APEX II diffractometer equipped with a Mo Kα INCOATEC ImuS micro-focus source ($\lambda = 0.71073$ Å). Indexing was performed using APEX4 (Difference Vectors method). Data integration and reduction were performed using SaintPlus. Absorption correction was performed by a multi-scan method implemented in SADABS. Space group was determined using XPREP implemented in APEX3. Structure was solved using SHELXT4 and refined using SHELXL-2018/3 (full-matrix least-squares on F2) through the OLEX2 interface program. The Ellipsoid plot was done with Platon. Remaining hydrogen atoms were refined using riding model. Enantiopure organic ligand was used for synthesis.

Powder X-ray diffraction

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance Diffractometer with Lynxeye detector using CuKα radiation. X-ray source operated at 40kV/40mA and Ni filter was used to suppress Beta radiation. 2.5 deg primary and secondary Soller slits were used to suppress axial divergence. Diffraction patterns were recorded from 2 to 60 2θ in variable slits mode and with knife edge installed. A typical scan rate was 20 sec/step with a step size of 0.02 deg.

Optical Spectroscopy

Optical diffuse-reflectance measurements were performed at room temperature using a Cary 5000 UV-Vis-NIR Spectrophotometer, coupled with an integrating sphere, from 200 to 2500 nm. $BaSO_4$ was used as a non-absorbing reflectance reference. The generated reflectance versus-wavelength data were used to estimate the band gap of the material by converting reflectance to absorbance data according to the Kubelka−Munk equation: $\alpha/S = (1-R)^2/2R$, where R is the reflectance and α and S are the absorption and scattering coefficients, respectively.

TGA-DSC measurements

Thermogravimetric Analysis (TGA) measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer. An amount of ~12 mg of sample was placed inside an Alumina Pan and heated up to 700 ºC under N_2 flow with a heating rate of 5 ºC/min. Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments Q20 Differential Scanning Calorimeter. An amount of 3 mg of sample was placed inside an Aluminium Pan and heated up to 250 ºC under N_2 flow with a heating rate of 5 ºC/min.

SEM/EDS Scanning Electron Microscopy

SEM measurements were recorded on a high-resolution thermal field emission source Hitachi SU-70. Data were acquired with an accelerating voltage of 16 kV. The EDS was performed with a Hitachi SU70 SEM using a IXRF SDD EDS system. The samples were prepared by pressing the powder on to a substrate of carbon adhesive tape and tilting the sample to 30 degrees. The electron beam energy was set to 16 KeV.

DRCD studies

Diffuse-reflectance CD (DRCD) studies were performed using a JASCO Model J-1500 Circular Dichroism Optical Rotatory Dispersion (CD/ ORD) spectrometer equipped with an integrating sphere and a xenon light source.

Magnetic Measurements

The magnetic measurements were performed using the vibrating sample magnetometry (VSM) option in the Physical Property Measurement System (PPMS) from Quantum Design. Sample mounting was done using a polypropylene powder holder and a brass tube as shown in Figure S11. Background signals were recorded prior to the measurements for both powdered samples. The temperature-dependent magnetization (M vs. T) was collected over a temperature span of 2-350 K, at a static magnetic field (H) of 0.1 T under a zero-field-cooled protocol. During this procedure, the samples, with known masses, were cooled in the absence of any external magnetic field. The temperature-dependent susceptibility (χ) was calculated using the equation $\chi = M/H$. The field-dependent magnetization (M vs. H) was measured from 9 to -9 T for temperatures ranging between 2 K and 300 K.

DFT Studies

We carried out spin-polarized density functional theory (DFT) calculations since the materials are found to be paramagnetic. For the geometry optimization, we used the plane-wave pseudopotential method as implemented in the Quantum ESPRESSO package.[10-11] The Kohn-Sham wave-functions and energies are calculated with the GGA-PBE[12-13] for electron exchange and correlation, using a plane-wave basis, with energy and charge density cutoffs of 40 and 320 Ry, respectively. The Grimme dispersion correction DFT-D3,[14-15] was used to account for the dispersion corrections. Ultrasoft pseudopotentials are used to describe the core-valence interactions.[16] The structural relaxation is performed until the force on each atom is smaller than 0.01 eV/Å. A k-point sampling of 4x4x4 was used for the Brillouin zone integration, following the Monkhorst-Pack scheme.[17]

The materials exhibit paramagnetism at room temperature and ferromagnetism at low temperature, as shown in the experimental magnetic studies section of the main manuscript. Since standard DFT is a 0K method, we treat these systems as ferromagnetic in our calculations. For accurate analysis of the electronic structure of these materials, we performed calculations with the hybrid functional HSE06, which consists of a 25% for the exact Fock exchange as implemented in the Crystal23 software package.[18-19] The latter is based on the expansion of the crystalline orbitals as a linear combination of a local basis set (BS) consisting of atomic-centered Gaussian orbitals, which allows faster calculations with hybrid functionals compared to plane-wave-based methods. The Cu, Cl, S, N, C, H atoms are described by the following triple-zeta valence basis sets: Cu_pob_TZVP_rev2, Cl_pob_TZVP_rev2, S_pob_TZVP_rev2, N_pob_TZVP_rev2, C_pob_TZVP_rev2, H_pob_TZVP_rev2, respectively (Taken form https://www.crystal.unito.it/basis_sets.html).

2. Synthesis

(THBTD)$_2$CuCl$_6$ (microcrystalline): 34 mg (0.25 mmol) of CuCl$_2$ were dissolved in a solution consisting of 1 mL of HCl, by heating under constant magnetic stirring. Then 85 mg (0.5 mmol) of THBTD linker were added to the hot solution. Heating was discontinued and the sample was left to cool to RT directly. Green crystals deposited after 10 min. They were collected by suction filtration and dried under vacuum overnight. Yield: 105 mg, (71% based on Cu).

(THBTD)$_2$CuCl$_6$ (large crystals): 136 mg (1 mmol) of CuCl$_2$ were dissolved in a solution consisting of 10 mL of HCl, by heating under constant magnetic stirring. Then 339 mg (2 mmol) of THBTD linker were added to the hot solution. Heating was discontinued and the sample was left to cool to RT directly. Green crystals are deposited after 1 day. They were collected by suction filtration and dried under vacuum overnight.

3. Characterization

SEM studies
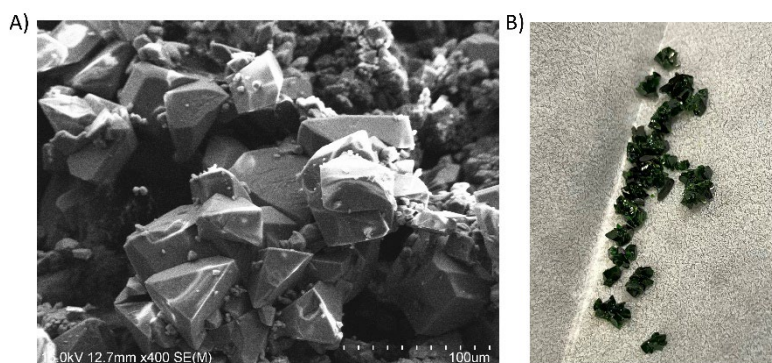
Figure S1. A) Representative SEM images and B) optical photograph of the fresh as-made (S-THBTD)$_2$CuCl$_6$ single crystals.

EDS measurements

Elt.	Line	Intensity (c/s)	Atomic %	Conc.	Units
C	Ka	0.00	0.000	0.000	wt.%
N	Ka	7.25	18.655	7.983	wt.%
O	Ka	3.51	2.932	1.433	wt.%
S	Ka	197.29	17.497	17.141	wt.%
Cl	Ka	509.40	52.218	56.557	wt.%
Cu	Ka	21.67	8.698	16.886	wt.%
			100.000	100.000	wt.% Total

kV   16.0
Takeoff Angle   60.0°
Elapsed Livetime 91.1

Cursor=11.835 keV 1 cnt ID = Hg lb1 Tl lb6 As kb2
Vert=5330   Window 0.005 - 40.955= 84,713 cnt

Figure S2. Representative EDS spectrum of fresh (S-THBTD)$_2$CuCl$_6$ single crystals. The Cl:Cu ratio is 6:1, matching exactly the formula derived from XRD studies.

X-ray diffraction measurements

Crystallographic tables

Table S1. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for (*R*-THBTD)$_2$CuCl$_6$ at 296.00 K with estimated standard deviations in parentheses.

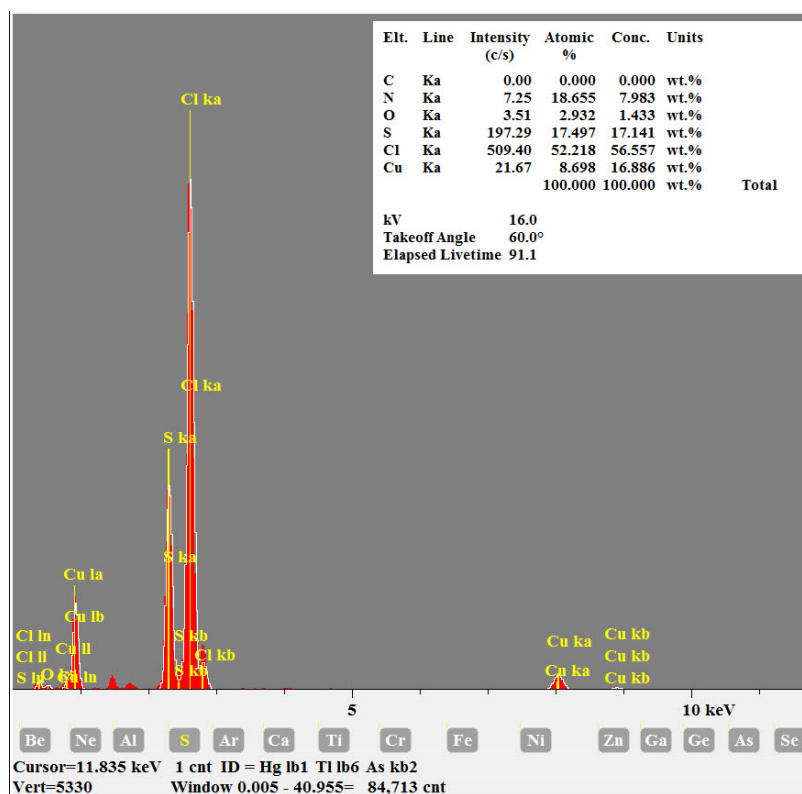| Label	x	y	z	Occupancy	U$_{eq}$*
Cu(1)	-1525(2)	1596(2)	-1074(2)	1	35(1)
S(2)	5850(2)	5845(2)	-1643(2)	1	42(1)
Cl(5)	5784(2)	7562(2)	4585(2)	1	50(1)
S(1)	11039(2)	7412(2)	9506(2)	1	41(1)
Cl(3)	337(2)	1650(2)	803(2)	1	63(1)
Cl(2)	-2825(2)	-431(2)	369(2)	1	58(1)
Cl(6)	11220(2)	5663(2)	13338(2)	1	52(1)
Cl(1)	-3493(2)	1653(2)	-2884(2)	1	59(1)
Cl(4)	-140(3)	3462(3)	-2608(3)	1	93(1)
C(8)	4089(9)	4897(9)	-2073(9)	1	37(2)
C(6)	12786(10)	10368(10)	5888(10)	1	48(2)
H(6D)	13995.63	10339.44	5700.55	1	58
H(6E)	12415.2	11434.45	5915.55	1	58
N(2)	13353(7)	9279(7)	8674(7)	1	40(2)
H(2)	14238.69	9812.99	8680.14	1	48
N(3)	9293(7)	8900(8)	3666(8)	1	43(2)
H(3A)	9318.29	9650.46	2847.37	1	51
H(3B)	8229.03	8653.32	3890	1	51
H3C()	9882.65	8068.4	3463.94	1	51
N(4)	3379(8)	5162(9)	-3424(8)	1	51(2)
H(4A)	2524.08	4644.37	-3594.22	1	61
H(4B)	3768.05	5852.85	-4142.18	1	61
C(4)	10044(8)	9450(8)	4998(7)	1	42(2)
H(4)	9455.76	10419.34	5154.98	1	50
C(14)	4622(8)	3771(8)	416(8)	1	34(2)
N(6)	7545(8)	4342(8)	4229(8)	1	50(2)
H(6A)	8595.93	4180.43	3902.14	1	60
H(6B)	7314.84	3623.32	5039.76	1	60
H6C()	7441.35	5279.15	4494.03	1	60

C(3)	9812(9)	8214(9)	6447(9)	1	42(2)
H(3D)	8672.89	8304.05	6852.15	1	50
H(3E)	9983.17	7183.96	6185.94	1	50
N(1)	13592(8)	8042(9)	11267(8)	1	49(2)
H(1A)	14498.31	8510.75	11393.72	1	58
H(1B)	13179.69	7400.4	12015.42	1	58
C(2)	11050(10)	8440(9)	7626(9)	1	38(2)
N(5)	3606(7)	3865(8)	-879(8)	1	39(2)
H(5)	2743.83	3303.54	-899.47	1	47
C(9)	5860(10)	4762(9)	219(9)	1	38(2)
C(10)	7077(9)	5002(9)	1425(9)	1	42(2)
H(10A)	7211.09	6102	1410.47	1	50
H(10B)	8172.27	4523.93	1245.34	1	50
C(5)	11883(7)	9763(8)	4612(6)	1	48(2)
H(5A)	11949.54	10518.1	3673.2	1	58
H(5B)	12458.06	8810.09	4425.27	1	58
C(7)	12377(9)	9360(9)	7388(9)	1	40(2)
C(12)	5847(8)	2598(7)	2912(6)	1	47(2)
H(12A)	5572.71	2069.33	3939.52	1	57
H(12B)	6780.02	2027.93	2509.45	1	57
C(1)	12827(9)	8312(9)	9908(9)	1	38(2)
C(13)	4319(11)	2666(10)	1876(10)	1	44(2)
H(13A)	4131.71	1640.49	1646.92	1	52
H(13B)	3320.83	3007.99	2398.09	1	52
C(11)	6337(8)	4246(7)	2966(7)	1	42(2)
H(11)	5306.26	4844.55	3158.29	1	50

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Anisotropic displacement parameters ($\text{Å}^2 \text{x} 10^3$) for (R-THBTD)$_2$CuCl$_6$ at 296.00 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	30(1)	45(1)	30(1)	-12(1)	-7(1)	2(1)
S(2)	37(1)	55(1)	31(1)	-19(1)	-5(1)	6(1)
Cl(5)	37(1)	66(2)	44(2)	-17(1)	-2(1)	-1(1)
S(1)	34(1)	57(2)	30(1)	-18(1)	-2(1)	5(1)
Cl(3)	58(2)	79(2)	48(2)	-36(1)	-28(1)	14(1)
Cl(2)	47(1)	65(1)	54(2)	-27(1)	-15(1)	20(1)

Cl(6)	44(1)	69(2)	39(2)	-16(1)	-5(1)	2(1)
Cl(1)	56(2)	75(2)	42(1)	-32(1)	-23(1)	14(1)
Cl(4)	63(2)	132(2)	66(2)	-62(2)	-26(2)	50(2)
C(8)	30(3)	46(4)	36(4)	-9(3)	-3(3)	-3(3)
C(6)	39(3)	63(4)	39(4)	-25(3)	-6(3)	10(3)
N(2)	33(3)	52(3)	32(3)	-18(3)	-2(2)	1(3)
N(3)	33(3)	60(4)	32(3)	-16(3)	-9(2)	8(3)
N(4)	39(3)	78(5)	33(4)	-22(3)	-10(3)	8(3)
C(4)	36(3)	57(4)	29(3)	-16(3)	-7(2)	6(3)
C(14)	33(3)	39(3)	26(3)	-5(3)	-2(3)	0(3)
N(6)	49(4)	60(4)	38(4)	-18(3)	-12(3)	5(3)
C(3)	37(3)	54(4)	33(4)	-22(3)	-7(3)	6(4)
N(1)	41(3)	67(4)	36(4)	-15(3)	-6(3)	-1(3)
C(2)	35(3)	45(4)	32(4)	-15(3)	-1(3)	7(3)
N(5)	31(3)	51(3)	36(3)	-15(2)	-7(2)	-6(3)
C(9)	36(3)	51(4)	24(4)	-12(3)	-4(3)	0(3)
C(10)	40(4)	50(4)	33(4)	-19(3)	-5(3)	3(3)
C(5)	40(3)	74(4)	28(2)	-25(3)	-5(2)	8(3)
C(7)	31(3)	53(4)	34(4)	-19(3)	-3(3)	-3(3)
C(12)	50(3)	52(3)	35(3)	-21(3)	-6(2)	11(2)
C(1)	30(3)	52(4)	31(4)	-6(3)	-2(3)	-4(3)
C(13)	49(4)	47(4)	34(3)	-23(3)	-2(3)	0(3)
C(11)	43(3)	52(3)	30(3)	-18(3)	-10(2)	3(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S3. Bond lengths [Å] for (R-THBTD)$_2$CuCl$_6$ at 296.00 K with estimated standard deviations in parentheses.

Label	Distances
Cu(1)-Cl(3)	2.247(2)
Cu(1)-Cl(2)	2.272(2)
Cu(1)-Cl(1)	2.247(2)
Cu(1)-Cl(4)	2.245(3)
S(2)-C(8)	1.734(8)
S(2)-C(9)	1.751(8)
S(1)-C(2)	1.747(9)
S(1)-C(1)	1.721(8)
C(8)-N(4)	1.308(10)
C(8)-N(5)	1.327(11)
C(6)-H(6D)	0.9700
C(6)-H(6E)	0.9700
C(6)-C(5)	1.524(10)
C(6)-C(7)	1.499(11)
N(2)-H(2)	0.8600
N(2)-C(7)	1.376(9)
N(2)-C(1)	1.332(11)
N(3)-H(3A)	0.8900
N(3)-H(3B)	0.8900
N(3)-H3C()	0.8900
N(3)-C(4)	1.486(8)
N(4)-H(4A)	0.8600
N(4)-H(4B)	0.8600
C(4)-H(4)	0.9800
C(4)-C(3)	1.541(10)
C(4)-C(5)	1.516(8)
C(14)-N(5)	1.399(9)

Symmetry transformations used to generate equivalent atoms:

Table S4. Bond angles [°] for (*R*-THBTD)$_2$CuCl$_6$ at 296.00 K with estimated standard deviations in parentheses.

Label	Angles
Cl(3)-Cu(1)-Cl(2)	91.06(9)
Cl(3)-Cu(1)-Cl(1)	176.31(12)
Cl(1)-Cu(1)-Cl(2)	89.02(8)
Cl(4)-Cu(1)-Cl(3)	89.97(9)
Cl(4)-Cu(1)-Cl(2)	175.37(15)
Cl(4)-Cu(1)-Cl(1)	90.25(9)
C(8)-S(2)-C(9)	90.1(4)
C(1)-S(1)-C(2)	90.5(4)
N(4)-C(8)-S(2)	123.2(6)
N(4)-C(8)-N(5)	125.5(7)
N(5)-C(8)-S(2)	111.3(6)
H(6D)-C(6)-H(6E)	108.4
C(5)-C(6)-H(6D)	110.0
C(5)-C(6)-H(6E)	110.0
C(7)-C(6)-H(6D)	110.0
C(7)-C(6)-H(6E)	110.0
C(7)-C(6)-C(5)	108.3(6)
C(7)-N(2)-H(2)	122.5
C(1)-N(2)-H(2)	122.5
C(1)-N(2)-C(7)	115.1(6)
H(3A)-N(3)-H(3B)	109.5
H(3A)-N(3)-H3C()	109.5
H(3B)-N(3)-H3C()	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for (S-THBTD)$_2$CuCl$_6$ at 296.15 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U$_{eq}$*
Cu(1)	11526(1)	8409(1)	11070(1)	1	30(1)
Cl(1)	13497(2)	8352(2)	12878(2)	1	49(1)
Cl(5)	4226(2)	2409(2)	5408(2)	1	43(1)
S(2)	-1035(2)	2591(2)	482(2)	1	36(1)
S(1)	4142(2)	4161(2)	11642(2)	1	35(1)
Cl(4)	12832(2)	10441(2)	9618(2)	1	48(1)
Cl(6)	-1225(2)	4364(2)	-3357(2)	1	44(1)
Cl(2)	10134(2)	6542(2)	12616(2)	1	70(1)
Cl(3)	9684(2)	8331(2)	9185(2)	1	52(1)
N(5)	-3348(5)	706(5)	1294(5)	1	32(1)
H(5)	-4226.33	164.26	1281.12	1	39
C(14)	-1056(7)	1552(6)	2354(6)	1	33(2)
C(13)	196(6)	1774(6)	3546(6)	1	35(2)
H(13A)	22.71	2812.06	3813.42	1	42
H(13B)	1332.43	1682.7	3137.06	1	42
N(3)	2469(5)	5662(5)	5774(5)	1	42(1)
H(3A)	2673.21	6411.42	4979.33	1	51
H(3B)	1417.06	5792.03	6112.14	1	51
H3C()	2601.43	4728.92	5481.25	1	51
N(6)	720(5)	1082(5)	6316(5)	1	36(1)
H(6A)	1779	1338.78	6090.08	1	43
H(6B)	705.99	321.64	7130.52	1	43
H6C()	122.46	1917.47	6525.53	1	43
N(2)	6371(5)	6156(5)	10871(5)	1	34(1)
H(2)	7231.96	6718.77	10888.03	1	41
N(4)	-3574(6)	1966(6)	-1272(5)	1	41(1)
H(4A)	-4477.56	1500.67	-1410.02	1	49
H(4B)	-3156.69	2618.69	-2010.71	1	49
N(1)	6605(6)	4843(6)	13421(5)	1	44(2)
H(1A)	7464.67	5358.16	13583.17	1	52
H(1B)	6217.92	4151.74	14141.84	1	52
C(12)	-27(5)	527(5)	4981(5)	1	32(1)
H(12)	563.95	-452.3	4820.08	1	38
C(1)	5890(6)	5111(6)	12085(6)	1	32(2)
C(7)	5364(6)	6255(6)	9578(6)	1	29(1)

Label					
C(9)	-2363(6)	628(6)	2593(6)	1	33(2)
C(6)	5668(7)	7351(6)	8137(7)	1	36(2)
H(6D)	6679.67	7008.47	7630.51	1	43
H(6E)	5835.33	8389.78	8365.35	1	43
C(10)	-2786(7)	-395(7)	4105(6)	1	41(2)
H(10A)	-2422.96	-1475.37	4078.66	1	49
H(10B)	-3993.85	-351.87	4292.21	1	49
C(8)	-2822(7)	1678(6)	87(6)	1	33(2)
C(11)	-1880(5)	214(5)	5369(4)	1	38(1)
H(11A)	-1943.48	-546.96	6307.49	1	45
H(11B)	-2453.5	1178.04	5558.36	1	45
C(5)	4168(5)	7410(5)	7078(4)	1	40(1)
H(5A)	3229.76	8002.87	7453.87	1	48
H(5B)	4467.12	7926.19	6052.63	1	48
C(3)	2930(6)	4993(6)	8589(6)	1	36(2)
H(3D)	1829.73	5471.63	8763.92	1	43
H(3E)	2809.91	3879.91	8612.46	1	43
C(2)	4115(7)	5250(6)	9777(7)	1	31(2)
C(4)	3667(5)	5753(5)	7029(4)	1	33(1)
H(4)	4693.18	5139.26	6835.4	1	39

$^*U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S6. Anisotropic displacement parameters ($\text{Å}^2\text{x}10^3$) for (S-THBTD)$_2$CuCl$_6$ at 296.15 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	26(1)	35(1)	28(1)	-8(1)	-5(1)	0(1)
Cl(1)	46(1)	61(1)	37(1)	-24(1)	-17(1)	9(1)
Cl(5)	32(1)	52(1)	43(1)	-12(1)	0(1)	-4(1)
S(2)	31(1)	46(1)	28(1)	-12(1)	-1(1)	3(1)
S(1)	32(1)	44(1)	28(1)	-14(1)	-4(1)	3(1)
Cl(4)	42(1)	49(1)	48(1)	-19(1)	-9(1)	12(1)
Cl(6)	39(1)	56(1)	36(1)	-10(1)	-2(1)	-1(1)
Cl(2)	49(1)	95(2)	54(1)	-42(1)	-15(1)	32(1)
Cl(3)	47(1)	65(1)	42(1)	-26(1)	-20(1)	8(1)
N(5)	27(2)	39(2)	31(2)	-11(2)	0(2)	-4(2)
C(14)	33(3)	40(3)	23(3)	-7(2)	-3(2)	0(2)
C(13)	31(3)	45(3)	29(3)	-13(2)	-7(2)	-2(2)

N(3)	41(2)	47(2)	37(2)	-13(2)	-8(2)	2(2)
N(6)	27(2)	50(2)	28(2)	-11(2)	-9(2)	4(2)
N(2)	28(2)	40(2)	34(2)	-10(2)	-3(2)	-5(2)
N(4)	32(2)	59(3)	30(2)	-11(2)	-6(2)	1(2)
N(1)	36(2)	60(3)	33(3)	-15(2)	-9(2)	2(2)
C(12)	28(2)	39(2)	27(2)	-7(2)	-4(2)	1(2)
C(1)	26(2)	37(3)	32(3)	-5(2)	-2(2)	-4(2)
C(7)	28(2)	31(2)	27(3)	-7(2)	-2(2)	-1(2)
C(9)	30(3)	41(3)	28(3)	-8(2)	-2(2)	-3(2)
C(6)	37(3)	37(2)	32(2)	-19(2)	2(2)	1(2)
C(10)	35(2)	51(3)	35(3)	-18(2)	-3(2)	1(2)
C(8)	27(2)	40(3)	31(3)	-3(2)	2(2)	-7(2)
C(11)	30(2)	55(2)	26(2)	-14(2)	-2(2)	2(2)
C(5)	44(2)	40(2)	32(2)	-15(2)	-5(2)	9(2)
C(3)	34(3)	36(3)	33(3)	-14(2)	-3(2)	6(2)
C(2)	30(3)	34(2)	28(3)	-9(2)	1(2)	3(2)
C(4)	33(2)	37(2)	26(2)	-9(2)	-6(2)	2(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S7. Bond lengths [Å] for (*S*-THBTD)$_2$CuCl$_6$ at 296.15 K with estimated standard deviations in parentheses.

Label	Distances
Cu(1)-Cl(1)	2.2516(15)
Cu(1)-Cl(4)	2.2750(16)
Cu(1)-Cl(2)	2.2504(17)
Cu(1)-Cl(3)	2.2503(15)
S(2)-C(14)	1.744(6)
S(2)-C(8)	1.726(6)
S(1)-C(1)	1.730(6)
S(1)-C(2)	1.754(6)
N(5)-H(5)	0.8600
N(5)-C(9)	1.393(7)
N(5)-C(8)	1.316(7)
C(14)-C(13)	1.504(8)
C(14)-C(9)	1.332(8)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(13)-C(12)	1.534(7)
N(3)-H(3A)	0.8900
N(3)-H(3B)	0.8900
N(3)-H3C()	0.8900
N(3)-C(4)	1.489(6)
N(6)-H(6A)	0.8900
N(6)-H(6B)	0.8900
N(6)-H6C()	0.8900
N(6)-C(12)	1.489(6)
N(2)-H(2)	0.8600
N(2)-C(1)	1.343(7)
N(2)-C(7)	1.396(7)
N(4)-H(4A)	0.8600
N(4)-H(4B)	0.8600
N(4)-C(8)	1.332(7)
N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600
N(1)-C(1)	1.300(7)
C(12)-H(12)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table S8. Bond angles [°] for (*S*-THBTD)$_2$CuCl$_6$ at 296.15 K with estimated standard deviations in parentheses.

Label	Angles
Cl(1)-Cu(1)-Cl(4)	88.96(6)
Cl(2)-Cu(1)-Cl(1)	90.29(6)
Cl(2)-Cu(1)-Cl(4)	175.31(9)
Cl(2)-Cu(1)-Cl(3)	89.98(6)
Cl(3)-Cu(1)-Cl(1)	175.59(7)
Cl(3)-Cu(1)-Cl(4)	91.13(6)
C(8)-S(2)-C(14)	89.9(3)
C(1)-S(1)-C(2)	91.0(3)
C(9)-N(5)-H(5)	122.8
C(8)-N(5)-H(5)	122.8
C(8)-N(5)-C(9)	114.4(4)
C(13)-C(14)-S(2)	123.2(4)
C(9)-C(14)-S(2)	111.2(4)
C(9)-C(14)-C(13)	125.5(5)
C(14)-C(13)-H(13A)	109.8
C(14)-C(13)-H(13B)	109.8
C(14)-C(13)-C(12)	109.5(4)
H(13A)-C(13)-H(13B)	108.2
C(12)-C(13)-H(13A)	109.8
C(12)-C(13)-H(13B)	109.8
H(3A)-N(3)-H(3B)	109.5
H(3A)-N(3)-H3C()	109.5
H(3B)-N(3)-H3C()	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for (*S*-THBTD)$_2$CuCl$_6$ at 100.00 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U$_{eq}$*
Cu(1)	11570(1)	8399(1)	11059(1)	1	15(1)
Cl(6)	-1201(2)	4375(2)	-3368(2)	1	22(1)
S(1)	4185(2)	4153(2)	11647(2)	1	17(1)
Cl(2)	9700(2)	8332(2)	9178(2)	1	24(1)
Cl(4)	13540(2)	8348(2)	12876(2)	1	22(1)

Cl(1)	10218(2)	6456(2)	12591(2)	1	31(1)
Cl(3)	12864(2)	10459(2)	9614(2)	1	23(1)
Cl(5)	4295(2)	2371(2)	5382(2)	1	20(1)
S(2)	-985(2)	2580(2)	450(2)	1	17(1)
C(12)	-2780(6)	1674(6)	51(6)	1	17(1)
N(2)	6417(5)	6167(5)	10863(5)	1	17(1)
H(2)	7297.81	6747.44	10875.74	1	20
C(2)	4152(7)	5256(6)	9793(6)	1	17(1)
N(4)	773(5)	1064(5)	6305(5)	1	20(1)
H(4A)	1869.95	1292.06	6079.43	1	24
H(4B)	724.64	302.48	7152.41	1	24
H4C()	177	1950.81	6505.17	1	24
N(1)	6664(5)	4831(5)	13421(5)	1	22(1)
H(1A)	7547.74	5355.51	13588.39	1	26
H(1B)	6269.33	4117.06	14158.81	1	26
C(7)	5396(6)	6258(5)	9585(6)	1	15(1)
N(5)	-3303(5)	675(5)	1277(5)	1	17(1)
H(5)	-4206.77	123.78	1266.41	1	20
C(3)	2957(6)	4988(6)	8575(6)	1	18(1)
H(3A)	1824.27	5476.81	8767.25	1	21
H(3B)	2847.45	3842.09	8579.73	1	21
N(6)	-3538(5)	1960(5)	-1302(5)	1	20(1)
H6C()	-4459.38	1474.86	-1441.24	1	24
H(6D)	-3119.99	2636.19	-2061.34	1	24
C(4)	3698(5)	5754(5)	7022(5)	1	19(1)
H(4)	4758.05	5128.53	6810.16	1	23
N(3)	2500(5)	5651(5)	5744(5)	1	21(1)
H3C()	2742.78	6387.81	4912.49	1	25
H(3D)	1419.51	5832.63	6082.07	1	25
H(3E)	2611.84	4669.14	5464.78	1	25
C(6)	5695(6)	7384(6)	8124(6)	1	19(1)
H(6A)	6726.1	7030.47	7578.87	1	23
H(6B)	5865.16	8450.87	8377.24	1	23
C(14)	267(6)	1734(6)	3518(6)	1	20(1)
H(14A)	89.94	2806.85	3802.4	1	23
H(14B)	1432.38	1628.59	3089.85	1	23
C(10)	-2715(7)	-436(6)	4072(6)	1	22(1)
H(10A)	-2330.56	-1547.03	4027.92	1	27

H(10B)	-3951.94	-397.39	4273.18	1	27
C(13)	-971(7)	1511(6)	2331(6)	1	18(1)
C(5)	4179(5)	7447(4)	7083(4)	1	21(1)
H(5A)	4469.13	7981.08	6028.23	1	25
H(5B)	3216.93	8051.52	7499.55	1	25
C(11)	-2305(6)	577(6)	2573(6)	1	18(1)
C(9)	-1820(5)	183(5)	5364(4)	1	20(1)
H(9A)	-2410.44	1180.21	5570.64	1	24
H(9B)	-1891.56	-595.71	6322.3	1	24
C(1)	5939(6)	5111(6)	12081(6)	1	16(1)
C(8)	36(5)	485(5)	4964(4)	1	17(1)
H(8)	644.77	-528.55	4791.25	1	21

$^*U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S10. Anisotropic displacement parameters ($\text{Å}^2\text{x}10^3$) for (S-THBTD)$_2$CuCl$_6$ at 100.00 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	13(1)	20(1)	12(1)	-5(1)	-3(1)	2(1)
Cl(6)	19(1)	31(1)	15(1)	-6(1)	-2(1)	2(1)
S(1)	15(1)	23(1)	12(1)	-8(1)	-2(1)	4(1)
Cl(2)	21(1)	29(1)	19(1)	-11(1)	-9(1)	5(1)
Cl(4)	21(1)	28(1)	16(1)	-10(1)	-7(1)	4(1)
Cl(1)	22(1)	41(1)	25(1)	-17(1)	-7(1)	16(1)
Cl(3)	18(1)	27(1)	21(1)	-7(1)	-5(1)	5(1)
Cl(5)	15(1)	28(1)	18(1)	-8(1)	-2(1)	1(1)
S(2)	14(1)	24(1)	12(1)	-7(1)	-1(1)	4(1)
C(12)	16(2)	20(2)	14(2)	-1(2)	4(2)	1(2)
N(2)	14(2)	21(2)	16(2)	-5(2)	-2(2)	-3(2)
C(2)	21(2)	17(2)	13(2)	-4(2)	-2(2)	0(2)
N(4)	12(2)	29(2)	17(2)	-8(2)	-6(2)	4(2)
N(1)	18(2)	31(2)	15(2)	-7(2)	-5(2)	4(2)
C(7)	15(2)	18(2)	11(2)	-2(2)	-3(2)	2(2)
N(5)	12(2)	22(2)	15(2)	-8(2)	-2(2)	1(2)
C(3)	17(2)	20(2)	15(2)	-7(2)	-3(2)	3(2)
N(6)	14(2)	32(2)	14(2)	-7(2)	-2(2)	0(2)
C(4)	20(2)	23(2)	15(2)	-8(2)	-6(2)	3(2)
N(3)	23(2)	25(2)	14(2)	-8(2)	-2(2)	3(2)

C(6)	19(2)	22(2)	15(2)	-10(2)	-1(2)	3(2)
C(14)	17(2)	25(2)	15(2)	-9(2)	-2(2)	4(2)
C(10)	21(2)	29(2)	15(2)	-12(2)	-2(2)	5(2)
C(13)	16(2)	25(2)	10(2)	-6(2)	0(2)	4(2)
C(5)	22(2)	24(2)	16(2)	-8(2)	-2(2)	5(2)
C(11)	17(2)	24(2)	12(2)	-7(2)	0(2)	-1(2)
C(9)	15(2)	31(2)	12(2)	-11(2)	-3(2)	5(2)
C(1)	12(2)	21(2)	16(2)	-4(2)	0(2)	-4(2)
C(8)	15(2)	24(2)	11(2)	-5(2)	-4(2)	5(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S11. Bond lengths [Å] for (*S*-THBTD)$_2$CuCl$_6$ at 100.00 K with estimated standard deviations in parentheses.

Label	Distances
Cu(1)-Cl(2)	2.2560(14)
Cu(1)-Cl(4)	2.2557(13)
Cu(1)-Cl(1)	2.2652(15)
Cu(1)-Cl(3)	2.2792(15)
S(1)-C(2)	1.747(6)
S(1)-C(1)	1.732(5)
S(2)-C(12)	1.727(6)
S(2)-C(13)	1.755(5)
C(12)-N(5)	1.335(6)
C(12)-N(6)	1.327(7)
N(2)-H(2)	0.8800
N(2)-C(7)	1.390(6)
N(2)-C(1)	1.346(7)
C(2)-C(7)	1.331(7)
C(2)-C(3)	1.498(7)
N(4)-H(4A)	0.9100
N(4)-H(4B)	0.9100
N(4)-H4C()	0.9100
N(4)-C(8)	1.488(6)
N(1)-H(1A)	0.8800
N(1)-H(1B)	0.8800
N(1)-C(1)	1.305(7)
C(7)-C(6)	1.498(7)
N(5)-H(5)	0.8800
N(5)-C(11)	1.391(6)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(4)	1.529(6)
N(6)-H6C()	0.8800

Symmetry transformations used to generate equivalent atoms:

Table S12. Bond angles [°] for (*S*-THBTD)$_2$CuCl$_6$ at 100.00 K with estimated standard deviations in parentheses.

Label	Angles
Cl(2)-Cu(1)-Cl(4)	176.38(6)
Cl(2)-Cu(1)-Cl(1)	89.80(5)
Cl(2)-Cu(1)-Cl(3)	91.28(5)
Cl(4)-Cu(1)-Cl(1)	90.14(5)
Cl(4)-Cu(1)-Cl(3)	88.99(5)
Cl(1)-Cu(1)-Cl(3)	176.48(7)
C(1)-S(1)-C(2)	90.5(2)
C(12)-S(2)-C(13)	90.5(2)
N(5)-C(12)-S(2)	111.3(4)
N(6)-C(12)-S(2)	123.7(4)
N(6)-C(12)-N(5)	125.0(5)
C(7)-N(2)-H(2)	123.0
C(1)-N(2)-H(2)	123.0
C(1)-N(2)-C(7)	114.0(4)
C(7)-C(2)-S(1)	111.2(4)
C(7)-C(2)-C(3)	125.4(5)
C(3)-C(2)-S(1)	123.3(4)
H(4A)-N(4)-H(4B)	109.5
H(4A)-N(4)-H4C()	109.5
H(4B)-N(4)-H4C()	109.5
C(8)-N(4)-H(4A)	109.5
C(8)-N(4)-H(4B)	109.5
C(8)-N(4)-H4C()	109.5
H(1A)-N(1)-H(1B)	120.0
C(1)-N(1)-H(1A)	120.0
C(1)-N(1)-H(1B)	120.0
N(2)-C(7)-C(6)	122.3(5)
C(2)-C(7)-N(2)	113.6(4)
C(2)-C(7)-C(6)	124.1(5)

Symmetry transformations used to generate equivalent atoms:

Table S13. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for (S-THBTD)$_2$CuCl$_6$ at 400.00 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U$_{eq}$*
Cu(1)	11577(2)	8419(2)	11078(2)	1	52(1)
S(1)	4196(2)	4175(2)	11640(2)	1	61(1)
Cl(2)	9742(3)	8339(3)	9192(3)	1	93(1)
Cl(6)	-1160(3)	4331(3)	-3341(3)	1	74(1)
Cl(3)	12885(3)	10440(3)	9632(3)	1	87(1)
S(2)	-980(2)	2602(2)	507(2)	1	60(1)
Cl(5)	4270(3)	2470(3)	5430(3)	1	74(1)
Cl(4)	13551(3)	8354(3)	12886(3)	1	89(1)
Cl(1)	10155(4)	6626(4)	12641(3)	1	131(2)
C(8)	-2763(11)	1701(10)	103(11)	1	55(2)
N(4)	-3520(10)	1958(10)	-1241(9)	1	71(2)
H(4A)	-4427.32	1490.72	-1365.19	1	85
H(4B)	-3106.31	2592.44	-1992.76	1	85
N(5)	-3295(8)	744(8)	1338(8)	1	56(2)
H(5)	-4181.9	213.39	1330.16	1	67
N(3)	2491(10)	5706(10)	5808(10)	1	82(2)
H(3A)	2856.06	6273.9	4941.64	1	99
H(3B)	1485.36	6072.91	6051.43	1	99
H3C()	2407.67	4731.82	5680.28	1	99
C(2)	4190(11)	5240(10)	9768(10)	1	54(2)
C(4)	3675(10)	5772(9)	7037(8)	1	62(2)
H(4)	4682.65	5165.12	6834.46	1	74
C(10)	234(11)	1809(11)	3569(9)	1	60(2)
H(10A)	57.57	2827.55	3828.57	1	73
H(10B)	1369.83	1733.94	3170.79	1	73
C(6)	5755(13)	7298(11)	8122(11)	1	67(2)
H(6A)	6743.42	6945.23	7613.26	1	81
H(6B)	5963.52	8316.16	8339.86	1	81
C(7)	5437(10)	6214(9)	9576(9)	1	52(2)
N(2)	6453(9)	6132(9)	10871(9)	1	58(2)
H(2)	7319.19	6687.84	10887.05	1	69
N(6)	769(8)	1126(9)	6333(8)	1	63(2)
H6C()	1816.16	1411.54	6096.48	1	76
H(6D)	783.48	369.81	7146.12	1	76

H(6E)	159.01	1928.62	6547.15	1	76
C(14)	-2331(10)	666(10)	2620(9)	1	56(2)
C(3)	2973(11)	5002(11)	8590(10)	1	63(2)
H(3D)	1882.31	5463.88	8779.78	1	76
H(3E)	2841.81	3907.75	8608.38	1	76
C(12)	-1829(8)	273(10)	5393(7)	1	65(2)
H(12A)	-2388.58	1226.23	5561.87	1	78
H(12B)	-1902.24	-471.91	6337.53	1	78
C(9)	-1001(11)	1584(10)	2382(10)	1	55(2)
C(13)	-2737(12)	-333(12)	4126(11)	1	67(2)
H(13A)	-2373.1	-1392.75	4111.27	1	81
H(13B)	-3942.71	-305.28	4307.54	1	81
N(1)	6661(10)	4851(10)	13417(9)	1	75(2)
H(1A)	7527.1	5354.59	13584.38	1	90
H(1B)	6261.25	4171.14	14137.51	1	90
C(5)	4232(11)	7380(9)	7082(8)	1	76(2)
H(5A)	3321.93	7971.45	7464.65	1	91
H(5B)	4520.56	7892.98	6055.39	1	91
C(11)	11(9)	570(9)	5008(8)	1	59(2)
H(11)	588.4	-393.74	4858.13	1	71
C(1)	5955(11)	5116(10)	12072(10)	1	56(2)

$^*U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S14. Anisotropic displacement parameters ($\text{Å}^2\text{x}10^3$) for (S-THBTD)$_2$CuCl$_6$ at 400.00 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	44(1)	66(1)	44(1)	-16(1)	-9(1)	3(1)
S(1)	53(2)	80(2)	45(2)	-26(1)	-7(1)	8(1)
Cl(2)	84(2)	116(2)	70(2)	-50(2)	-38(2)	17(2)
Cl(6)	61(2)	100(2)	55(2)	-23(2)	-7(1)	2(2)
Cl(3)	69(2)	97(2)	82(2)	-38(1)	-20(2)	29(2)
S(2)	49(1)	83(2)	43(2)	-24(1)	-4(1)	6(1)
Cl(5)	54(2)	100(2)	65(2)	-25(1)	-4(1)	-2(2)
Cl(4)	82(2)	114(2)	62(2)	-48(2)	-33(2)	23(2)
Cl(1)	90(2)	191(3)	86(2)	-85(2)	-31(2)	64(2)
C(8)	45(4)	68(5)	50(5)	-6(3)	0(3)	-5(3)
N(4)	59(4)	108(6)	43(4)	-20(4)	-11(3)	-2(4)

N(5)	42(3)	74(4)	50(4)	-21(3)	-3(3)	0(3)
N(3)	73(5)	103(6)	64(5)	-33(4)	-19(4)	12(4)
C(2)	47(4)	70(5)	43(4)	-14(4)	-4(3)	-6(4)
C(4)	65(4)	74(4)	43(3)	-24(3)	-12(3)	6(3)
C(10)	55(4)	79(5)	42(4)	-29(4)	-12(4)	12(4)
C(6)	69(5)	72(5)	55(5)	-35(4)	-2(4)	9(3)
C(7)	47(4)	60(4)	44(4)	-11(3)	-5(3)	6(3)
N(2)	51(3)	73(4)	49(4)	-22(3)	-7(3)	-7(3)
N(6)	50(4)	87(5)	46(4)	-25(3)	-18(3)	11(3)
C(14)	44(4)	76(5)	46(5)	-27(4)	-5(3)	-5(4)
C(3)	55(5)	74(5)	58(5)	-26(4)	-2(4)	-1(4)
C(12)	51(3)	98(5)	41(3)	-32(3)	-5(2)	10(3)
C(9)	50(4)	69(5)	40(4)	-26(4)	-4(3)	11(3)
C(13)	55(4)	91(5)	51(4)	-34(4)	-9(3)	8(4)
N(1)	61(4)	106(6)	53(4)	-30(4)	-16(3)	8(4)
C(5)	80(5)	86(5)	55(4)	-34(4)	-11(4)	16(3)
C(11)	49(4)	80(4)	44(3)	-20(3)	-10(3)	5(3)
C(1)	45(4)	77(5)	46(4)	-17(4)	-9(3)	-3(4)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S15. Bond lengths [Å] for (*S*-THBTD)$_2$CuCl$_6$ at 400.00 K with estimated standard deviations in parentheses.

Label	Distances
Cu(1)-Cl(2)	2.242(3)
Cu(1)-Cl(3)	2.276(3)
Cu(1)-Cl(4)	2.247(3)
Cu(1)-Cl(1)	2.237(3)
S(1)-C(2)	1.754(10)
S(1)-C(1)	1.730(9)
S(2)-C(8)	1.719(9)
S(2)-C(9)	1.742(9)
C(8)-N(4)	1.320(11)
C(8)-N(5)	1.332(12)
N(4)-H(4A)	0.8600
N(4)-H(4B)	0.8600
N(5)-H(5)	0.8600
N(5)-C(14)	1.367(10)
N(3)-H(3A)	0.8900
N(3)-H(3B)	0.8900
N(3)-H3C()	0.8900
N(3)-C(4)	1.458(11)
C(2)-C(7)	1.324(11)
C(2)-C(3)	1.477(13)
C(4)-H(4)	0.9800
C(4)-C(3)	1.531(11)
C(4)-C(5)	1.505(10)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-C(9)	1.489(13)
C(10)-C(11)	1.537(11)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(6)-C(7)	1.486(11)
C(6)-C(5)	1.522(13)
C(7)-N(2)	1.400(11)

Symmetry transformations used to generate equivalent atoms:

Table S16. Bond angles [°] for (*S*-THBTD)$_2$CuCl$_6$ at 400.00 K with estimated standard deviations in parentheses.

Label	Angles
Cl(2)-Cu(1)-Cl(3)	91.18(11)
Cl(2)-Cu(1)-Cl(4)	175.21(16)
Cl(4)-Cu(1)-Cl(3)	89.03(10)
Cl(1)-Cu(1)-Cl(2)	90.25(11)
Cl(1)-Cu(1)-Cl(3)	173.57(19)
Cl(1)-Cu(1)-Cl(4)	90.07(11)
C(1)-S(1)-C(2)	90.5(4)
C(8)-S(2)-C(9)	90.4(4)
N(4)-C(8)-S(2)	124.3(7)
N(4)-C(8)-N(5)	124.9(8)
N(5)-C(8)-S(2)	110.8(7)
C(8)-N(4)-H(4A)	120.0
C(8)-N(4)-H(4B)	120.0
H(4A)-N(4)-H(4B)	120.0
C(8)-N(5)-H(5)	122.4
C(8)-N(5)-C(14)	115.2(7)
C(14)-N(5)-H(5)	122.4
H(3A)-N(3)-H(3B)	109.5
H(3A)-N(3)-H3C()	109.5
H(3B)-N(3)-H3C()	109.5
C(4)-N(3)-H(3A)	109.5
C(4)-N(3)-H(3B)	109.5
C(4)-N(3)-H3C()	109.5
C(7)-C(2)-S(1)	110.5(6)
C(7)-C(2)-C(3)	126.4(8)
C(3)-C(2)-S(1)	123.1(6)
N(3)-C(4)-H(4)	106.9
N(3)-C(4)-C(3)	111.0(6)
N(3)-C(4)-C(5)	113.4(7)
C(3)-C(4)-H(4)	106.9

Symmetry transformations used to generate equivalent atoms:

Table S17. Crystal data and structure refinement for (*R*-THBTD)$_2$CuCl$_6$ - 1 year at 296 K.

Formula weight	618.77
Temperature	296 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions	a = 7.9384(2) Å, α = 80.3760(10)° b = 8.6810(2) Å, β = 88.8120(10)° c = 8.8260(2) Å, γ = 87.3700(10)°
Volume	598.98(2) Å^3
Z	1
Density (calculated)	1.715 g/cm^3
Absorption coefficient	9.210 mm^{-1}
F(000)	315
Crystal size	0.11 x 0.08 x 0.08 mm^3
θ range for data collection	5.083 to 72.176°
Index ranges	-9<=h<=9, -10<=k<=10, -10<=l<=10
Reflections collected	8983
Independent reflections	4054 [R$_{int}$ = 0.0254]
Completeness to θ = 67.679°	98.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4054 / 3 / 265
Goodness-of-fit	0.990
Final R indices [I > 2σ(I)]	R$_{obs}$ = 0.0270, wR$_{obs}$ = 0.0711
R indices [all data]	R$_{all}$ = 0.0284, wR$_{all}$ = 0.0725
Extinction coefficient	.
Largest diff. peak and hole	0.488 and -0.254 e·Å^{-3}

Table S18. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for (*R*-THBTD)$_2$CuCl$_6$ - 1 year at 296 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U$_{eq}$*
Cu(1)	-1537(1)	1618(2)	-1076(2)	1	30(1)
Cl(6)	11214(2)	5672(2)	13346(2)	1	44(1)
S(1)	11019(2)	7436(2)	9508(2)	1	36(1)
Cl(4)	310(2)	1698(2)	806(2)	1	53(1)
S(2)	5846(2)	5865(2)	-1646(2)	1	36(1)
Cl(3)	-2844(2)	-415(2)	371(2)	1	48(1)
Cl(2)	-3510(2)	1678(2)	-2886(2)	1	50(1)
Cl(5)	5762(2)	7613(2)	4584(2)	1	43(1)
Cl(1)	-146(2)	3485(2)	-2627(2)	1	71(1)
N(4)	7526(6)	4367(6)	4220(6)	1	43(2)
H(4A)	8576.04	4190.75	3896.73	1	51
H(4B)	7290.64	3651.77	5034.18	1	51
H4C()	7429.09	5314.86	4479.14	1	51
N(6)	3381(6)	5180(7)	-3428(6)	1	44(2)
H(6A)	2519.76	4668.92	-3593.47	1	53
H(6B)	3771.47	5870.47	-4147.33	1	53
C(7)	9794(6)	8253(6)	6442(6)	1	35(2)
H(7A)	8654.66	8340.32	6847.18	1	42
H(7B)	9971.18	7218.44	6172.65	1	42
N(5)	3611(5)	3871(5)	-879(6)	1	34(1)
H(5)	2752.38	3305.57	-898.96	1	41
C(14)	5865(7)	4773(7)	220(7)	1	32(2)
C(9)	6325(5)	4270(5)	2964(5)	1	34(1)

H(9)	5296.47	4879.43	3157.2	1	41
C(11)	4303(7)	2667(7)	1869(7)	1	38(2)
H(11A)	4131.21	1632.98	1635.27	1	45
H(11B)	3296.19	3007.84	2383.84	1	45
N(2)	13335(5)	9319(5)	8691(6)	1	34(1)
H(2)	14213.67	9860.96	8701.59	1	40
C(4)	12357(6)	9401(6)	7408(6)	1	33(2)
C(13)	4095(6)	4910(6)	-2088(7)	1	33(2)
C(12)	4618(6)	3779(6)	422(6)	1	30(1)
N(3)	9271(5)	8943(6)	3675(5)	1	37(1)
H(3A)	9269.8	9704.66	2863.64	1	45
H(3B)	8217.92	8671.35	3908.28	1	45
H3C()	9879.51	8118.83	3457.42	1	45
C(10)	5827(6)	2611(5)	2914(5)	1	41(1)
H(10A)	5545.07	2089.9	3941.42	1	49
H(10B)	6761.98	2027.26	2522.49	1	49
C(5)	12817(6)	8338(6)	9909(7)	1	32(2)
N(1)	13561(6)	8063(7)	11258(6)	1	43(2)
H(1A)	14457.1	8538.63	11397.67	1	51
H(1B)	13149.1	7407.76	11996.9	1	51
C(6)	11033(7)	8474(6)	7635(7)	1	33(2)
C(2)	11866(5)	9811(6)	4625(5)	1	40(1)
H(2A)	12440	8852.26	4428.49	1	48
H(2B)	11935.14	10577.93	3693.42	1	48
C(3)	12765(8)	10403(8)	5903(7)	1	42(2)
H(3D)	13973.26	10363.29	5714.99	1	50

H(3E)	12403.25	11480.92	5931.13	1	50
C(15)	7067(6)	5030(6)	1414(6)	1	36(2)
H(15A)	7188.71	6139.5	1394.91	1	44
H(15B)	8165.81	4551.45	1237.42	1	44
C(8)	10018(5)	9500(5)	5005(5)	1	34(1)
H(8)	9425.19	10475.6	5166.07	1	40

$^*U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S19. Anisotropic displacement parameters ($Å^2 x 10^3$) for (R-THBTD)$_2$CuCl$_6$ - 1 year at 296 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	27(1)	37(1)	26(1)	-7(1)	-5(1)	-1(1)
Cl(6)	40(1)	57(1)	35(1)	-10(1)	-3(1)	-2(1)
S(1)	30(1)	48(1)	27(1)	-12(1)	-2(1)	2(1)
Cl(4)	50(1)	67(1)	41(1)	-26(1)	-21(1)	8(1)
S(2)	33(1)	45(1)	27(1)	-14(1)	-4(1)	3(1)
Cl(3)	42(1)	51(1)	46(1)	-18(1)	-9(1)	11(1)
Cl(2)	47(1)	63(1)	35(1)	-24(1)	-19(1)	9(1)
Cl(5)	32(1)	55(1)	42(1)	-12(1)	-2(1)	-4(1)
Cl(1)	51(1)	99(2)	52(1)	-42(1)	-17(1)	32(1)
N(4)	40(2)	53(3)	34(2)	-12(2)	-9(2)	0(2)
N(6)	38(2)	64(3)	29(2)	-14(2)	-11(2)	4(2)
C(7)	33(2)	44(3)	27(3)	-13(2)	-7(2)	0(2)
N(5)	31(2)	39(2)	32(2)	-8(2)	-4(2)	-5(2)

C(14)	32(2)	40(2)	23(3)	-6(2)	-1(2)	2(2)
C(9)	34(2)	42(2)	26(2)	-12(2)	-7(2)	0(2)
C(11)	39(2)	38(2)	35(3)	-18(2)	0(2)	1(2)
N(2)	27(2)	43(2)	31(2)	-12(2)	-2(2)	-5(2)
C(4)	29(2)	42(3)	30(3)	-11(2)	-2(2)	-4(2)
C(13)	28(2)	40(3)	33(3)	-6(2)	-2(2)	-6(2)
C(12)	28(2)	36(2)	26(2)	-4(2)	-4(2)	-3(2)
N(3)	30(2)	49(2)	29(2)	-12(2)	-8(2)	7(2)
C(10)	47(2)	39(2)	33(2)	-12(2)	-5(2)	7(2)
C(5)	27(2)	42(3)	26(3)	1(2)	-2(2)	-4(2)
N(1)	35(2)	61(3)	32(3)	-10(2)	-5(2)	-3(2)
C(6)	32(2)	39(2)	29(3)	-10(2)	-2(2)	1(2)
C(2)	35(2)	56(2)	25(2)	-16(2)	-4(2)	3(2)
C(3)	39(3)	52(3)	33(3)	-18(2)	-5(2)	-1(2)
C(15)	34(2)	41(3)	32(3)	-14(2)	-3(2)	5(2)
C(8)	30(2)	44(2)	26(2)	-8(2)	-5(2)	0(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S20. Bond lengths [Å] for (*R*-THBTD)$_2$CuCl$_6$ - 1 year at 296 K with estimated standard deviations in parentheses.

Label	Distances
Cu(1)-Cl(4)	2.2492(15)
Cu(1)-Cl(3)	2.2761(17)
Cu(1)-Cl(2)	2.2531(14)
Cu(1)-Cl(1)	2.2536(18)
S(1)-C(5)	1.730(6)
S(1)-C(6)	1.746(6)
S(2)-C(14)	1.758(6)
S(2)-C(13)	1.735(6)
N(4)-H(4A)	0.8900
N(4)-H(4B)	0.8900
N(4)-H4C()	0.8900
N(4)-C(9)	1.493(6)
N(6)-H(6A)	0.8600
N(6)-H(6B)	0.8600
N(6)-C(13)	1.303(8)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-C(6)	1.497(8)
C(7)-C(8)	1.537(7)
N(5)-H(5)	0.8600
N(5)-C(13)	1.339(8)
N(5)-C(12)	1.402(7)

Symmetry transformations used to generate equivalent atoms:

Table S21. Bond angles [°] for (R-THBTD)$_2$CuCl$_6$ - 1 year at 296 K with estimated standard deviations in parentheses.

Label	Angles
Cl(4)-Cu(1)-Cl(3)	91.31(6)
Cl(4)-Cu(1)-Cl(2)	175.58(8)
Cl(4)-Cu(1)-Cl(1)	90.00(6)
Cl(2)-Cu(1)-Cl(3)	88.96(6)
Cl(1)-Cu(1)-Cl(3)	175.18(10)
Cl(1)-Cu(1)-Cl(2)	90.09(7)
C(5)-S(1)-C(6)	90.3(3)
C(13)-S(2)-C(14)	90.6(3)
H(4A)-N(4)-H(4B)	109.5
H(4A)-N(4)-H4C()	109.5
H(4B)-N(4)-H4C()	109.5
C(9)-N(4)-H(4A)	109.5
C(9)-N(4)-H(4B)	109.5
C(9)-N(4)-H4C()	109.5
H(6A)-N(6)-H(6B)	120.0
C(13)-N(6)-H(6A)	120.0
C(13)-N(6)-H(6B)	120.0
H(7A)-C(7)-H(7B)	108.2
C(6)-C(7)-H(7A)	109.7
C(6)-C(7)-H(7B)	109.7
C(6)-C(7)-C(8)	109.7(4)
C(8)-C(7)-H(7A)	109.7

Symmetry transformations used to generate equivalent atoms:
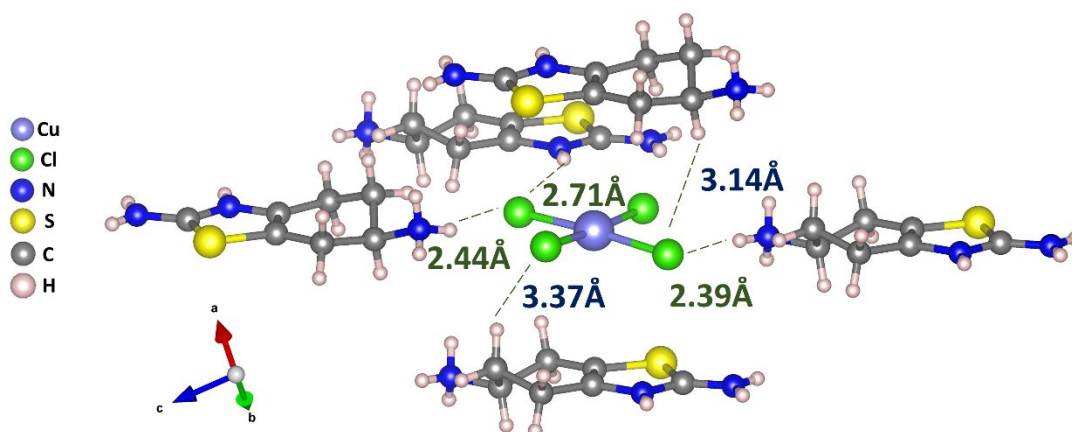
Figure S3. Part of the crystal structure of the (*R*-THBTD)$_2$CuCl$_6$ showcasing the number and magnitude of hydrogen bonds in-plane strongly impose a square planar coordination geometry.
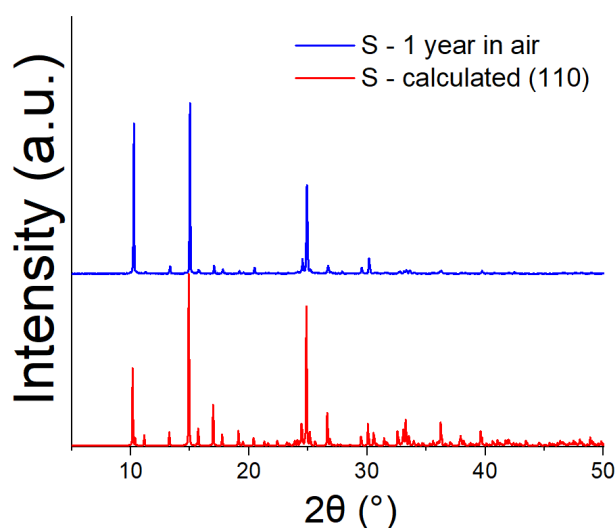
Figure S4. Comparison of the PXRD patterns of the 1-year air-treated (*S*-THBTD)$_2$CuCl$_6$ compound with the calculated pattern derived from the corresponding solved single-crystal structure, accounting for preferred orientation (110).
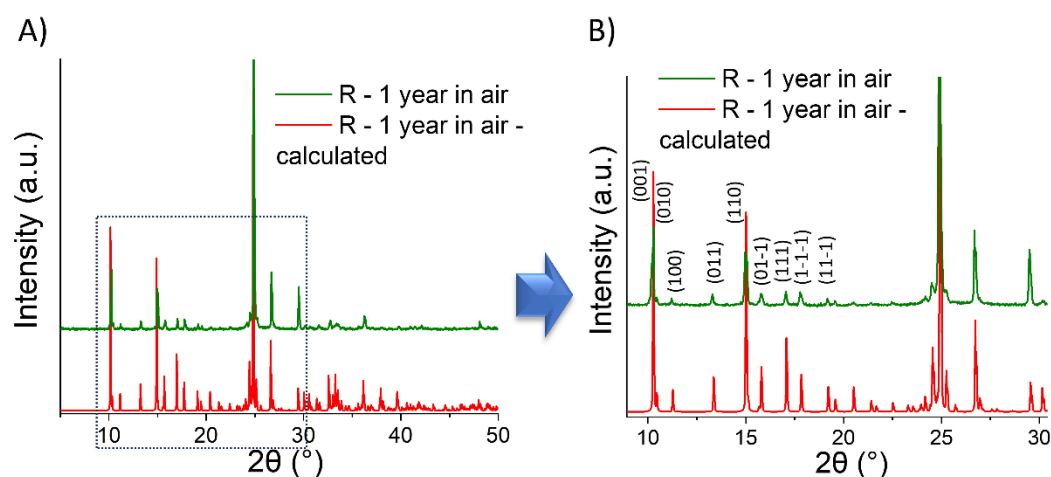
Figure S5. A) Comparison of the PXRD patterns for the 1-year air-treated (*R*-THBTD)$_2$CuCl$_6$ compound to the calculated pattern derived from the corresponding solved single-crystal structure. B) Zoom into the highlighted area of A). There is no appearance of additional diffraction peaks indicative of material decomposition.

Thermogravimetric analysis
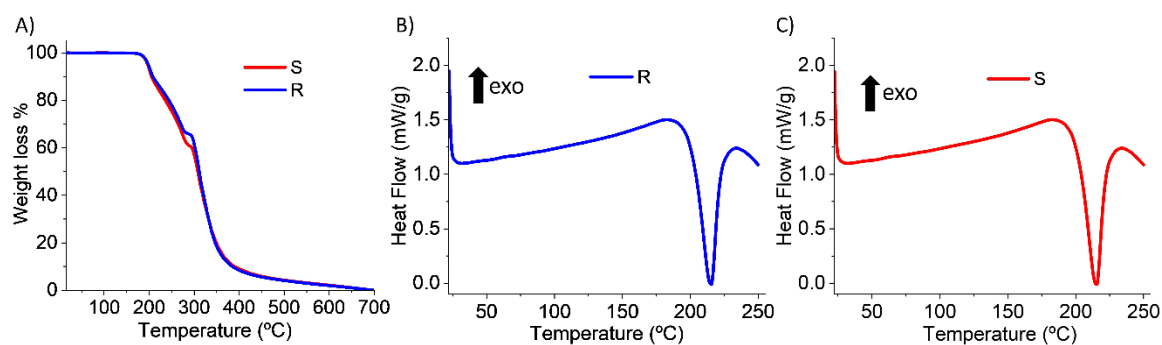
Figure S6. A) TGA curves for the dried as made (*R*-THBTD)$_2$CuCl$_6$ and (*S*-THBTD)$_2$CuCl$_6$ crystals, B) DSC curve for the dried (*R*-THBTD)$_2$CuCl$_6$ and C) (*S*-THBTD)$_2$CuCl$_6$ as made crystals exhibiting one endothermic peak.

UV-Vis studies
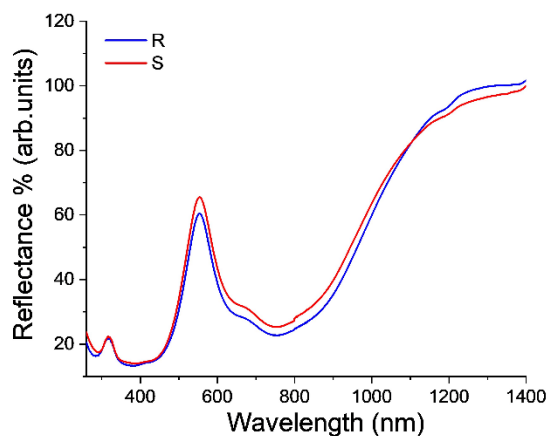
Figure S7. UV-Vis diffuse reflectance spectra of the fresh (*S*-THBTD)$_2$CuCl$_6$ and (*R*-THBTD)$_2$CuCl$_6$ materials.
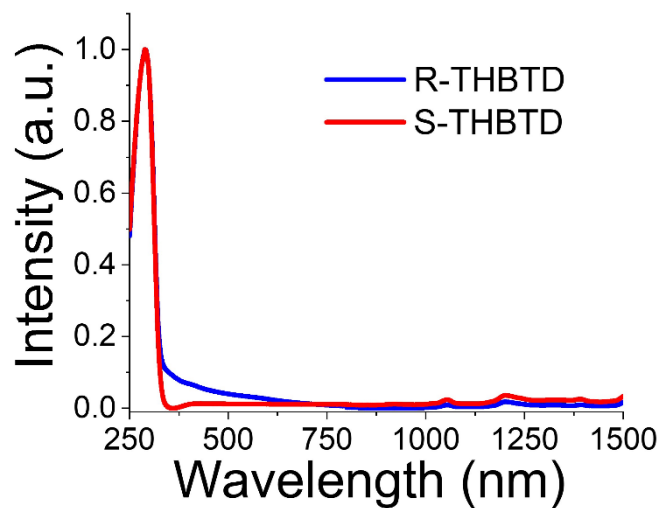
Figure S8. The absorbance spectra of the chiral *R*-THBTD and *S*-THBTD organic molecules.
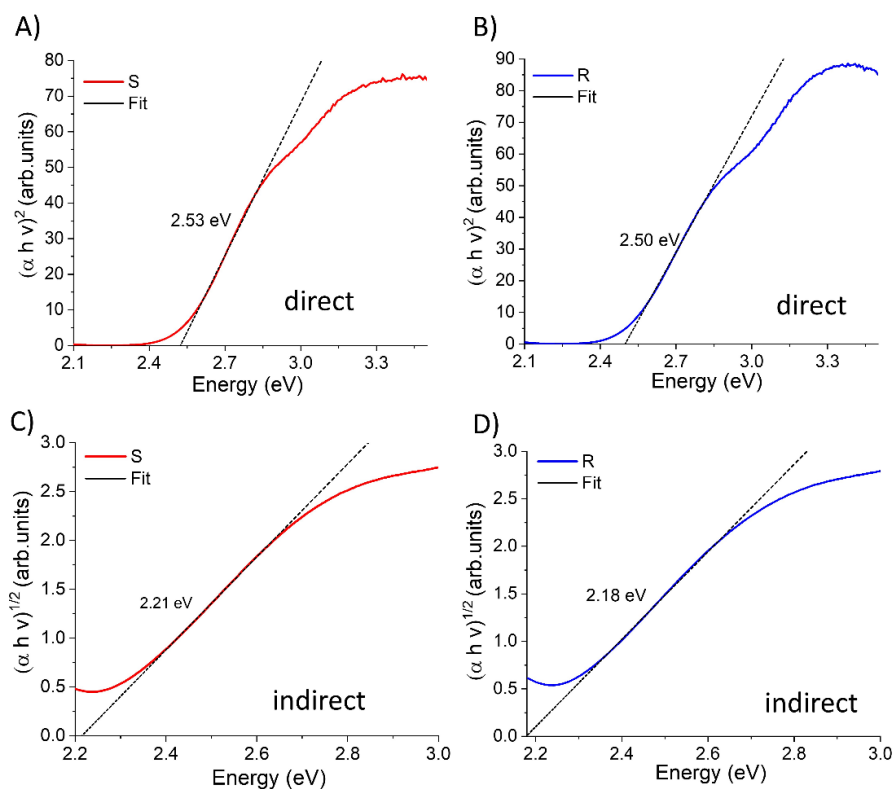
Figure S9. Tauc plots and determined band gap considering a direct allowed transition for the A) (*S*-THBTD)$_2$CuCl$_6$ and B) (*R*-THBTD)$_2$CuCl$_6$ enantiomers and indirect allowed transition for the C) (*S*-THBTD)$_2$CuCl$_6$ and d) (*R*-THBTD)$_2$CuCl$_6$ analogs respectively.
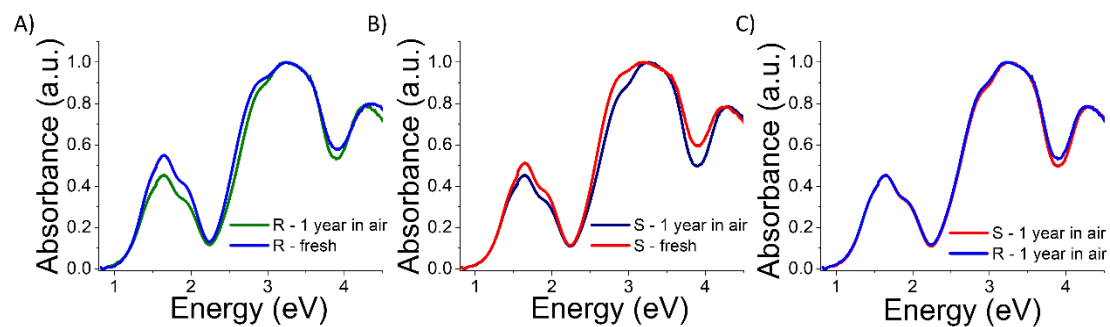
Figure S10. A) comparison of the optical absorption spectra for the fresh and the one after one-year of air exposure (*R*-THBTD)$_2$CuCl$_6$ and B) (*S*-THBTD)$_2$CuCl$_6$ enantiomers. C) Comparison of the optical absorption spectra for the one-year air-treated samples, demonstrating the robustness of the optical properties.

Table S22. Bond angles [°] and bond lengths (Å) for the fresh and 1-year air-treated (*R*-THBTD)$_2$CuCl$_6$ sample with estimated standard deviations in parentheses.

Bonds: Cu-Cl (Å)	Fresh R	1 year in air R
	2.245(3)	2.2492(15)
	2.272(2)	2.2761(17)
	2.247(2)	2.2531(14)
	2.247(2)	2.2536(18)
Angles: Cl-Cu-Cl (°)		
	91.06(9)	91.31(6)
	176.31(12)	175.58(8)
	89.02(8)	90.00(6)
	89.97(9)	88.96(6)
	175.37(15)	175.18(10)
	90.25(9)	90.09(7)

Magnetic studies
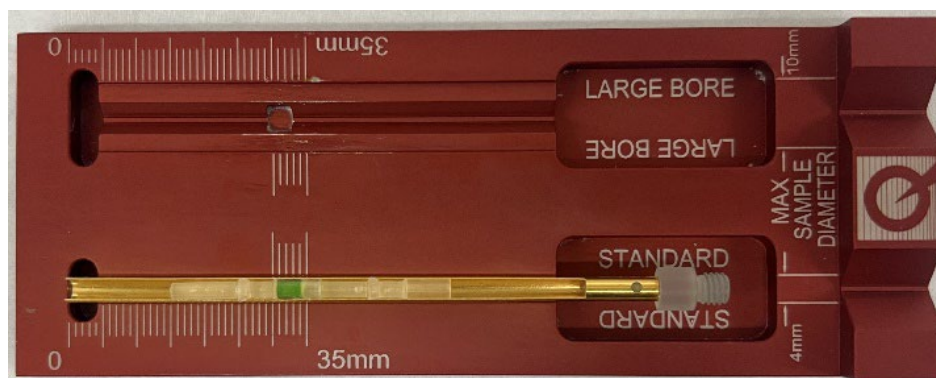
Figure S11. Sample mounting set up for the (*S*-THBTD)$_2$CuCl$_6$ powdered sample.
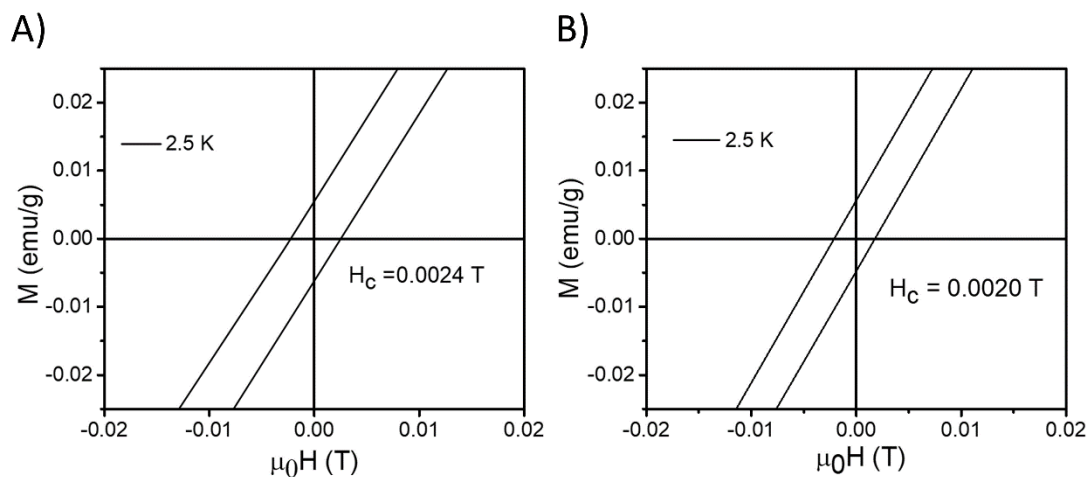
Figure S12. Enlarged magnetic hysteresis (M-H) loops show the presence of clear magnetic hysteresis, which is a typical characteristic for a ferromagnet, at low temperatures (e.g., 2.5 K) for A) (*S*-THBTD)$_2$CuCl$_6$ and B) (*R*-THBTD)$_2$CuCl$_6$ samples.
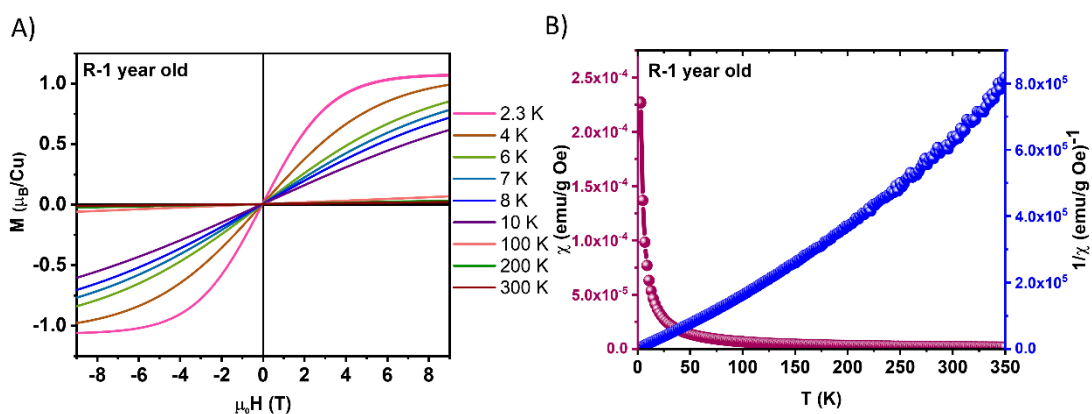

Figure S13. A) Magnetic-field dependent magnetization (M-H) curves and B) Temperature-dependent magnetic susceptibility (χ) for the 1-year air-treated (*R*-THBTD)$_2$CuCl$_6$ sample.

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