Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2023

Supporting Information for

A pair of ionic 1D Cu(II) chain enantiomers simultaneously displaying large second- and third-harmonic generation responses

Xiaodi Du,* Congli Gao, Zhiqiang Zhang, Bing Su and Xi-Li Li*

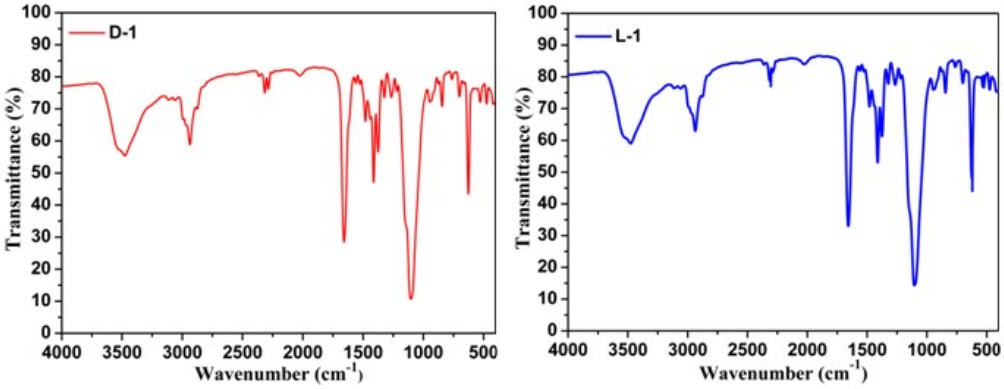

Fig. S1 IR spectra of **D-1** and **L-1**. The broad banks at 3472 (3741) cm^{-1} are attributed to the O–H stretching vibrations of H_2O molecule; the strong peaks at 1661 (1662) cm^{-1} originate from the C=O stretching vibrations of aldehyde group in DMF molecules; the strong peaks at 1101 cm^{-1} and 628 cm^{-1} are the asymmetric and symmetric stretching vibrations of ClO_4^- groups.

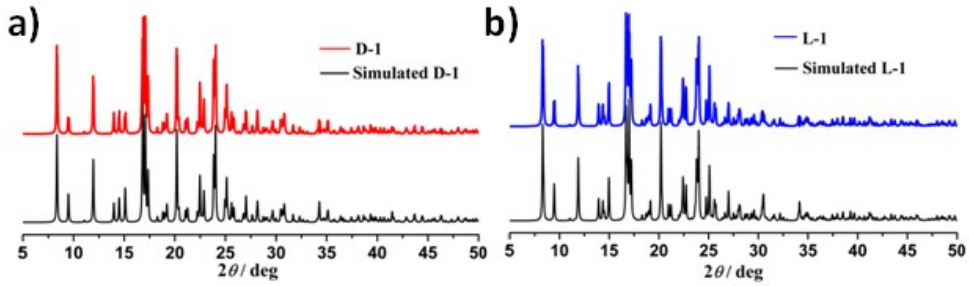

Fig. S2 a) Experimental and simulated PXRD patterns of **D-1** polycrystalline sample. b) Experimental and simulated PXRD patterns of **L-1** polycrystalline sample.

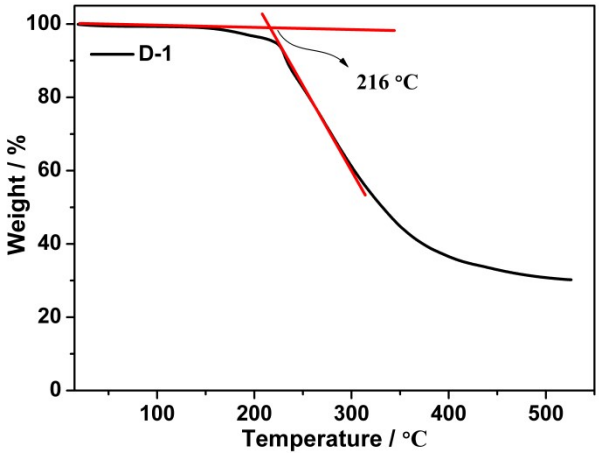

Fig. S3 Thermogravimetric analyses of **D-1**.

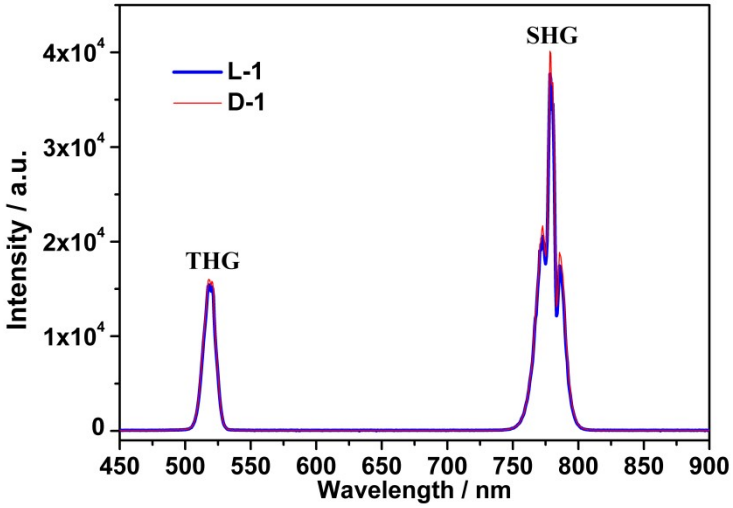

Fig. S4 THG and SHG spectra of **D-1** and **L-1** based on crystal samples under excitation at λ = 1550 nm with T_{int} = 0.5 s at room temperature.

Table S1 Crystallographic data and structure refinement parameters for **D-1/L-1** enantiomeric pairs

Complexes	**D-1**	**L-1**
Chemical formula	$C_{21}H_{29}N_5O_{10}Cl_2Cu$	$C_{21}H_{29}N_5O_{10}Cl_2Cu$
Formula weight	645.93	645.93
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.3721(2)	10.4203(3)
b (Å)	12.2081(3)	12.3268(3)
c (Å)	21.1481(5)	21.0653(6)
$\alpha = \beta = \gamma$ (deg)	90	90
V(Å^3)	2677.85(10)	2705.82(13)
Z	4	4
D_c(g cm^{-3})	1.602	1.586
μ (mm^{-1})	1.078	1.067
F(000)	1332	1332
Reflections collected	7278	7908
Independent reflections	5006	4905
Data/restraints/parameters	5006/2/365	4905/2/362
GOF	1.096	0.996
R_1 [$I >= 2\sigma$ (I)][a]	0.0621	0.0528
wR_2 [$I >= 2\sigma$ (I)][b]	0.1527	0.1113
Flack parameter	0.002(12)	0.001(13)
CCDC	2269485	2269487

[a] $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$. [b] $_wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) for **D-1/L-1**

Bond lengths for **D-1**

Cu(1)─O(1)	2.377(7)	Cu(1)─O(10)	1.974(6)	Cu(1)─N(1)	1.990(6)
Cu(1)─N(2)	2.010(6)	Cu(1)─N(4)	2.016(7)	Cu(1)─N(3A)	2.601(7)

Symmetry Codes for A: $-x + 1/2, -y, z + 1/2$

Bond lengths for **L-1**

Cu(1)─O(1)	2.398(5)	Cu(1)─O(10)	1.958(4)	Cu(1)─N(1)	1.990(5)
Cu(1)─N(2)	2.014(5)	Cu(1)─N(4)	2.012(6)	Cu(1)─N(3A)	2.588(6)

Symmetry Codes for A: $-x + 1/2, -y, z + 1/2$

Table S3 Selected bond angles (°) for **D-1/L-1**

Bond angles for **D-1**

N(1)-Cu(1)-N(2)	81.9(2)	N(4)-Cu(1)-N(2)	97.6(3)	O(10)-Cu(1)-N(4)	89.5(3)
O(10)-Cu(1)-N(1)	91.2(2)	O(1)-Cu(1)-N(3A)	171.67(3)		

Symmetry Codes for A: $-x + 1/2, -y, z + 1/2$

Bond angles for **L-1**

N(1)-Cu(1)-N(2)	81.9(2)	N(4)-Cu(1)-N(2)	97.6(2)	O(10)-Cu(1)-N(4)	90.1(2)
O(10)-Cu(1)-N(1)	90.9(2)	O(1)-Cu(1)-N(3A)	170.41(2)		

Symmetry Codes for A: $-x + 1/2, -y, z + 1/2$

Table S4 Calculated dipole moments of ionic **D-1** and molecular $[Cu(L_R)(NO_3)_2]_n$

Compound	**D-1**	$[Cu(L_R)(NO_3)_2]_n$
μ_{total} (D)	33.3972	17.6732
X	26.9433	–11.6804
Y	–18.7848	12.7715
Z	–6.0466	–3.5777