Supporting Information

The Power of Heterometalation through Lithium for Helix Chain-Based Noncentrosymmetric Metal-Organic Frameworks with Tunable Second-Harmonic Generation Effects

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Materials and Methods. All chemicals were obtained from commercial sources and used without further purification. Thermogravimetric analyses (TGA) were carried out on a NETSCHZ STA-449C thermal analyzer at a ramp rate of 5 °C min^{-1} in nitrogen and air atmosphere. Powder X-ray diffraction (PXRD) studies were carried out with a Japan Rigaku D/Max2550VB+/PC diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å).

Synthesis of $\{[Zn(HBTC)(H_2O)]\}_n$ (SNNU-71). A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.03 g, 0.1 mmol), $LiCl{\cdot}H_2O$ (0.012 g, 0.2 mmol), H_3BTC (0.021 g, 0.1 mmol), and DMF/DMP (v/v = 1/1) 4 mL was added in a 20 mL vial, while stirring at room temperature. After a few minutes, the mixed solution was sealed, heated at 100 °C for 4 days, and then slowly cooled to room temperature. Colorless rod-like crystals of as-synthesized **SNNU-71** were collected in 52% yield based on Zn(II).

Synthesis of $\{Li_4[Cd_2(HBTC)(BTC)_2]\}_n$ (SNNU-72). A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.031 g, 0.1 mmol), $LiCl{\cdot}H_2O$ (0.018 g, 0.3 mmol), H_3BTC (0.021 g, 0.1 mmol), and 4 mL DMF was added in a 20 mL vial, while stirring at room temperature. After a few minutes, the mixed solution was sealed, heated at 100 °C for 5 days, and then slowly cooled to room temperature. Colorless rod-like crystals of **SNNU-72** were collected in 68% yield based on Cd(II).

Synthesis of $\{CoLi(BTC)(DMA)_2\}_n$ (SNNU-73). A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.058 g, 0.2 mmol), $LiCl{\cdot}H_2O$ (0.018 g, 0.3 mmol), H_3BTC (0.042 g, 0.2 mmol), and 4 mL DMA was added in a 20 mL vial, while stirring at room temperature. After a few minutes, the mixed solution was sealed, heated at 100 °C for 4 days, and then slowly cooled to room temperature. Purple octahedral-like crystals of as-synthesized **SNNU-73** were collected in 68% yield based on Co(II).

Synthesis of $\{CdLi_2(BTC)_{4/3}(H_2O)_3\}_n$ (SNNU-74). A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.031 g, 0.1 mmol), $LiCl{\cdot}H_2O$ (0.018 g, 0.3 mmol), H_3BTC (0.021 g, 0.1 mmol), 2 mL DMA, and 2 mL 1,4-dioxane was added in a 20 mL vial, while stirring at room temperature. After a few minutes, the mixed solution was sealed, heated at 100 °C for 6 days, and then slowly cooled to room temperature. Colorless block crystals of as-synthesized **SNNU-74** were collected in 48% yield based on Cd(II).

Synthesis of $\{Li_2[Zn_3Li_5(BTC)_4(MTAZ)(H_2O)_4]\}_n$ (SNNU-75). A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.03 g, 0.1 mmol), $LiCl{\cdot}H_2O$ (0.006 g, 0.1 mmol), H_3BTC (0.042 g, 0.2 mmol), MTAZ (0.017 g, 0.2 mmol), 2 mL DMA, and 2 mL methanol was added in a 20 mL vial, while stirring at room temperature. After a few minutes, the mixed

solution was sealed, heated at 100 °C for 5 days, and then slowly cooled to room temperature. Colorless block crystals of as-synthesized **SNNU-75** were collected in 45% yield based on Zn(II).

X-ray Crystallographic Determination. Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SADABS program was used for absorption correction. All structures were solved by direct methods using the SHELXS-97 program and refined by the SHELXL-97 program.[S1-S3] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The large volume fractions of solvents and solvent cations in the lattice pores could not be modeled in terms of atomic sites and were treated using the SQUEEZE routine in the PLATON software package.[S4] The detailed crystallographic data and the structure refinement parameters of compounds are summarized in Table 1 and Table S1-S2. Selected bond lengths are given in Table S3.

Gas Adsorption. Gas sorption isotherms were measured on a Micromeritics ASAP 2020 HD88 surface-area and pore-size analyzer up to 1 atm of gas pressure by the static volumetric method. All used gases were of 99.99% purity. Prior to sorption analysis, dichloromethane-exchanged samples were loaded into the sample tube and dried at 60-120 °C by using the “outgas” function of the surface area analyzer. The gas sorption isotherms for N_2, H_2, and CO_2 were measured.

Second-Harmonic Generation. Powder second-harmonic generation (SHG) measurements were performed on the basis of the Kurtz−Perry method at 298 K.[S5] The measurements were carried out with a Q-switched Nd:YAG laser at a wavelength of 1064 nm. Polycrystalline samples were ground and sieved into a series of distinct size ranges: 0.040−0.060 mm, 0.060−0.080 mm, 0.080−0.125 mm, 0.125−0.150 mm, 0.150−0.200 mm, and 0.200−0.300 mm which were pressed between glass slides and secured with tape in 1-mm-thick aluminum holders containing a hole 8 mm in diameter. Each of them was then placed into a light-tight box, and the intensity of the frequency-doubled output emitted from the samples was collected through a photomultiplier tube. Crystalline KH_2PO_4 (KDP) as the reference was ground and sieved into the same particle size ranges. The ratios of the SHG signals of componds **SNNU-71**, **SNNU-72**, **SNNU-74**, and **SNNU-75** to the reference were calculated based on the intensity of second harmonic outputs in the same particle size range of 0.080−0.125 mm.

Table S1. Crystal data and structure refinements for **SNNU-71**, **-72** and **-73**.

Compound	**SNNU-71**	**SNNU-72**	**SNNU-73**
Empirical formula	$C_9H_6O_7Zn$	$C_{27}H_{14}Cd_2O_{18}$	$C_{17}H_{21}CoLiN_2O_8$
Formula weight	291.51	851.18	447.23
Crystal system	Hexagonal	Orthorhombic	Tetragonal
Space group	*P*6(1)	*P*2(1)2(1)2(1)	*P*4(1)2(1)2
a (Å)	21.436(8)	16.0672(13)	13.2699(3)
b (Å)	21.436(8)	17.2692(15)	13.2699(3)
c (Å)	13.767(8)	22.649(2)	17.6469(10)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	120	90	90
V (Å^3)	5479(4)	6284.4(9)	3106(2)
Z	6	4	4
D_{calcd}(Mg·m^{-3})	0.530	0.900	0.956
μ(mm^{-1})	0.678	0.717	0.582
F(000)	876	1664	924
ϑ for data collection (deg)	2.19 to 25.02	2.50 to 24.99	3.07 to 26.36
Reflections collected/unique	23055/6352	31378 / 11047	10035/3180
R(int)	0.1358	0.1376	0.0815
parameters	154	424	133
GOF on F^2	1.045	0.828	1.128
R_1[a], wR_2 [I > 2δ (I)]	0.0573, 0.1193	0.0613, 0.1187	0.0789, 0.2211
R_1, wR_2 (all data)	0.0849, 0.1229	0.1015, 0.1296	0.0816, 0.2243
ρ_{fin}(max/min) (e·Å^{-3})	0.397/-0.287	1.088/-0.712	0.871/-0.522
Flack parameter	0.11(2)	0.07(4)	0.02(4)

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table S2. Crystal data and structure refinements for **SNNU-74** and **-75**.

Compound	**SNNU-74**	**SNNU-75**
Empirical formula	$C_{12}H_{10}CdLi_2O_{11}$	$C_{38}H_{15}Li_5N_4O_{28}Zn_3$
Formula weight	456.48	1206.35
Crystal system	Hexagonal	Trigonal
Space group	*R*3*c*	*P*3(2)21
a (Å)	31.0217(6)	23.7899(8)
b (Å)	31.0217(6)	23.7899(8)
c (Å)	16.2941(7)	13.1159(10)
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	120
V (Å^3)	13579.8(7)	6428.6(6)
Z	18	3
D_{calcd}(Mg·m^{-3})	1.005	0.935
μ(mm^{-1})	0.754	1.471
F(000)	4032	1800
ϑ for data collection (deg)	3.21 to 26.37	3.72 to 72.48
Reflections collected/unique	17994/4967	16970 / 8140
R(int)	0.0378	0.0844
parameters	235	354
GOF on F^2	1.046	0.965
R_1[a], wR_2 [I > 2δ (I)]	0.0478, 0.1220	0.0671, 0.1735
R_1, wR_2 (all data)	0.0544, 0.1256	0.0867, 0.1850
ρ_{fin}(max/min) (e·Å^{-3})	0.868/-1.282	0.439/-0.387
Flack parameter	-0.02(4)	0.02(4)

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table S3.Selected bond lengths (Å) and angles (°) for the compounds **SNNU-71-75.**

SNNU-71			
Zn(1)-O(5)	1.921(4)	O(5)-Zn(1)-O(1)	112.17(14)
Zn(1)-O(1)	1.966(4)	O(3)-Zn(1)-O(1)	123.32(16)
Zn(1)-O(3)	1.951(4)	O(5)-Zn(1)-O(7)	105.09(18)
Zn(1)-O(7)	2.028(4)	O(3)-Zn(1)-O(7)	96.17(16)
O(5)-Zn(1)-O(3)	116.16(14)	O(1)-Zn(1)-O(7)	98.29(17)
SNNU-72			
Cd(1)-O(10a)	2.256(6)	O(17c)-Cd(1)-O(2)	90.0(2)
Cd(1)-O(5b)	2.289(6)	O(7)-Cd(1)-O(2)	118.1(2)
Cd(1)-O(17c)	2.295(6)	O(1)-Cd(1)-O(2)	52.2(2)
Cd(1)-O(7)	2.337(5)	O(15d)-Cd(2)-O(12e)	94.9(3)
Cd(1)-O(1)	2.388(6)	O(15d)-Cd(2)-O(14)	106.9(2)
Cd(1)-O(2)	2.487(6)	O(12e)-Cd(2)-O(14)	121.5(2)
Cd(2)-O(15d)	2.254(6)	O(15d)-Cd(2)-O(13)	161.7(2)
Cd(2)-O(12e)	2.279(6)	O(12e)-Cd(2)-O(13)	98.1(2)
Cd(2)-O(14)	2.359(6)	O(14)-Cd(2)-O(13)	55.1(2)
Cd(2)-O(13)	2.361(5)	O(15d)-Cd(2)-O(3)	87.4(2)
Cd(2)-O(3)	2.375(7)	O(12e)-Cd(2)-O(3)	141.8(3)
Cd(2)-O(4)	2.446(6)	O(14)-Cd(2)-O(3)	93.9(2)
Cd(2)-O(11e)	2.592(6)	O(13)-Cd(2)-O(3)	90.4(2)
O(10a)-Cd(1)-O(5b)	88.6(2)	O(15d)-Cd(2)-O(4)	105.3(2)
O(10a)-Cd(1)-O(17c)	173.3(2)	O(12e)-Cd(2)-O(4)	89.4(2)
O(5b)-Cd(1)-O(17c)	85.5(2)	O(14)-Cd(2)-O(4)	132.3(2)
O(10a)-Cd(1)-O(7)	92.8(2)	O(13)-Cd(2)-O(4)	87.8(2)
O(5b)-Cd(1)-O(7)	107.7(2)	O(3)-Cd(2)-O(4)	53.6(2)
O(17c)-Cd(1)-O(7)	92.0(2)	O(15d)-Cd(2)-O(11e)	88.1(2)
O(10a)-Cd(1)-O(1)	90.6(2)	O(12e)-Cd(2)-O(11e)	53.4(2)
O(5b)-Cd(1)-O(1)	81.9(2)	O(14)-Cd(2)-O(11e)	73.4(2)
O(17c)-Cd(1)-O(1)	85.5(2)	O(13)-Cd(2)-O(11e)	89.3(2)
O(10a)-Cd(1)-O(2)	91.8(2)	O(3)-Cd(2)-O(11e)	164.5(2)
O(5b)-Cd(1)-O(2)	134.1(2)	O(4)-Cd(2)-O(11e)	141.8(2

Symmetry codes: a) x - 1/2, - y + 3/2, - z + 1; b) - x, y + 1/2, - z + 3/2; c) - x + 1, y + 1/2, - z + 3/2; d) x - 1/2, - y + 1/2, - z +1; e) x, y - 1, z; f) - x, y - 1/2, - z + 3/2; g) x + 1/2, - y + 3/2, - z + 1; h) x, y + 1,z; i) x + 1/2, - y + 1/2, - z + 1; j) - x + 1, y - 1/2, - z + 3/2.

SNNU-73

Co/Li(1)-O(1a)	1.924(3)	O(1a)-Co/Li(1)-O(3b)	110.30(17)
Co/Li(1)-O(2)	1.917(3)	O(2)-Co/Li(1)-O(3b)	110.44(17)
Co/Li(1)-O(3b)	1.948(3)	O(1a)-Co/Li(1)-O(4)	98.15(18)
Co/Li(1)-O(4)	1.984(3)	O(2)-Co/Li(1)-O(4)	110.24(16)
O(1a)-Co/Li(1)-O(2)	120.36(17)	O(3b)-Co/Li(1)-O(4)	105.86(17)

Symmetry codes: a) y, x, - z; b) y - 1/2, - x + 3/2, z - 1/4; c) - y + 2, - x + 2, - z + 1/2; d) - y + 3/2 , x + 1/2, z + 1/4.

SNNU-74

Cd(1)-O(9a)	2.151(5)	O(5)-Cd(1)-O(8)	103.41(18)
Cd(1)-O(6b)	2.203(5)	O(9a)-Cd(1)-O(10)	94.5(2)
Cd(1)-O(5)	2.305(5)	O(6b)-Cd(1)-O(10)	86.5(2)
Cd(1)-O(8)	2.314(5)	O(5)-Cd(1)-O(10)	152.6(2)
Cd(1)-O(10)	2.425(5)	O(8)-Cd(1)-O(10)	53.74(18)
Li(1)-O(4b)	1.891(12)	O(4b)-Li(1)-O(3)	118.0(6)
Li(1)-O(3)	1.891(12)	O(4b)-Li(1)-O(7a)	104.1(6)
Li(1)-O(7a)	1.912(13)	O(3)-Li(1)-O(7a)	115.9(6)
Li(1)-O(5)	2.035(12)	O(4b)-Li(1)-O(5)	104.6(5)
Li(2)-O(2)	1.802(19)	O(3)-Li(1)-O(5)	112.8(6)
Li(2)-O(8)	1.902(13)	O(7a)-Li(1)-O(5)	99.2(5)
Li(2)-O(1)	1.91(2)	O(2)-Li(2)-O(8)	111.6(10)
Li(2)-O(11)	2.006(14)	O(2)-Li(2)-O(1)	112.4(9)
O(9a)-Cd(1)-O(6b)	113.6(2)	O(8)-Li(2)-O(1)	108.5(8)
O(9a)-Cd(1)-O(5)	111.25(18)	O(2)-Li(2)-O(11)	113.1(9)
O(6b)-Cd(1)-O(5)	91.34(18)	O(8)-Li(2)-O(11)	94.3(6)
O(9a)-Cd(1)-O(8)	118.7(2)	O(1)-Li(2)-O(11)	115.4(9)
O(6b)-Cd(1)-O(8)	114.4(2)		

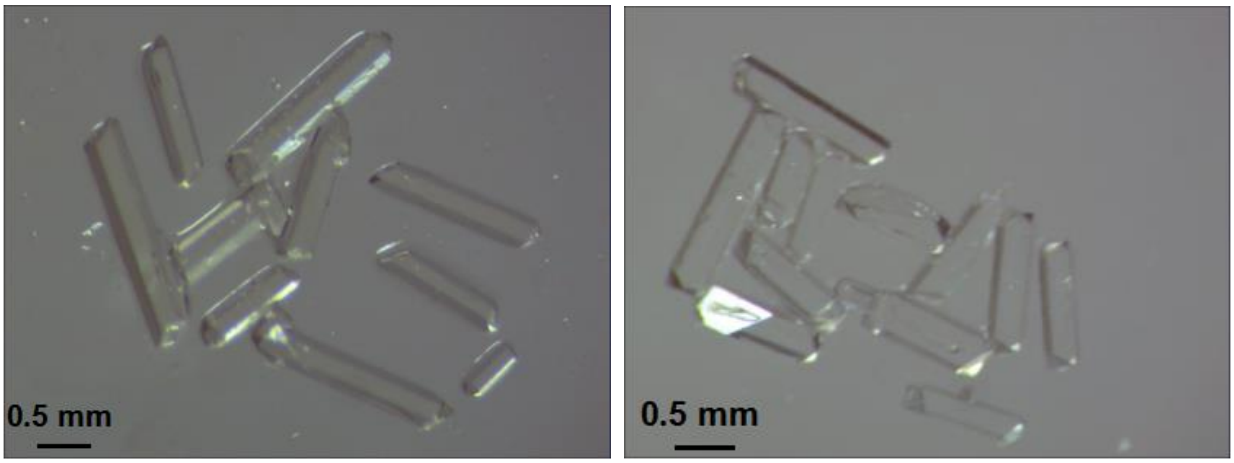
Symmetry codes: a) - y - 4/3, x - y - 2/3, z + 1/3; b) - y - 4/3, - x - 5/3, z - 1/6; c) - x + y - 1, - x - 2, z; d) - y - 2, x - y - 1, z; e) - y - 5/3, - x - 4/3, z + 1/6; f) - x + y - 2/3, - x - 4/3, z - 1/3.

SNNU-75

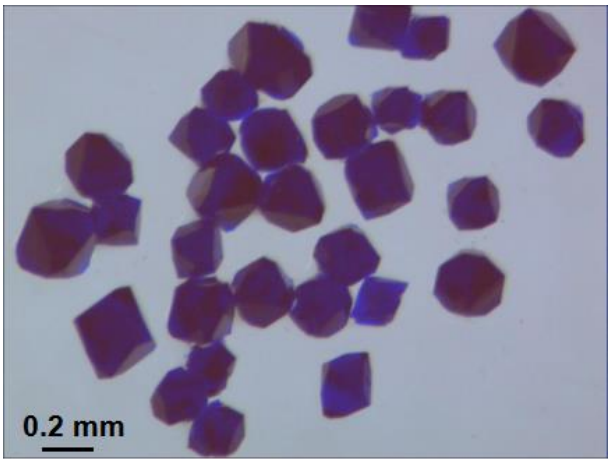
Zn(1)-O(12)	1.913(5)	O(10)-Zn(1)-N(1)	101.5(2)
Zn(1)-O(5)	1.929(4)	O(3)-Zn(2)-O(3a)	128.1(2)
Zn(1)-O(10)	1.940(4)	O(3)-Zn(2)-O(1a)	107.0(2)
Zn(1)-N(1)	2.003(6)	O(3a)-Zn(2)-O(1a)	105.74(18)
Zn(2)-O(3)	1.958(4)	O(3)-Zn(2)-O(1)	105.74(18)
Zn(2)-O(3a)	1.958(4)	O(3a)-Zn(2)-O(1)	107.0(2)

Zn(2)-O(1a)	1.963(4)	O(1a)-Zn(2)-O(1)	99.7(3)
Zn(2)-O(1)	1.963(4)	O(11)-Li(1)-O(8)	107.2(6)
Li(1)-O(11)	1.880(12)	O(11)-Li(1)-O(2)	111.9(6)
Li(1)-O(8)	1.913(12)	O(8)-Li(1)-O(2)	109.0(6)
Li(1)-O(2)	1.918(12)	O(11)-Li(1)-O(13)	105.7(6)
Li(1)-O(13)	1.958(14)	O(8)-Li(1)-O(13)	106.4(6)
Li(2)-O(14)	1.920(19)	O(2)-Li(1)-O(13)	116.2(7)
Li(2)-O(4b)	1.926(15)	O(14)-Li(2)-O(4b)	103.9(9)
Li(2)-O(7)	1.950(13)	O(14)-Li(2)-O(7)	111.5(7)
Li(2)-O(6c)	1.961(12)	O(4b)-Li(2)-O(7)	110.1(7)
Li(3)-O(9)	1.897(6)	O(14)-Li(2)-O(6c)	103.3(8)
Li(3)-O(9d)	1.897(6)	O(4b)-Li(2)-O(6c)	110.7(6)
Li(3)-O(4b)	1.987(7)	O(7)-Li(2)-O(6c)	116.4(8)
Li(3)-O(4c)	1.987(7)	O(9)-Li(3)-O(9d)	109.2(5)
O(12)-Zn(1)-O(5)	108.5(2)	O(9)-Li(3)-O(4b)	116.34(18)
O(12)-Zn(1)-O(10)	117.7(2)	O(9d)-Li(3)-O(4b)	107.04(17)
O(5)-Zn(1)-O(10)	124.9(2)	O(9)-Li(3)-O(4c)	107.04(17)
O(12)-Zn(1)-N(1)	95.4(3)	O(9d)-Li(3)-O(4c)	116.34(18)
O(5)-Zn(1)-N(1)	102.3(2)	O(4b)-Li(3)-O(4c)	101.0(4)

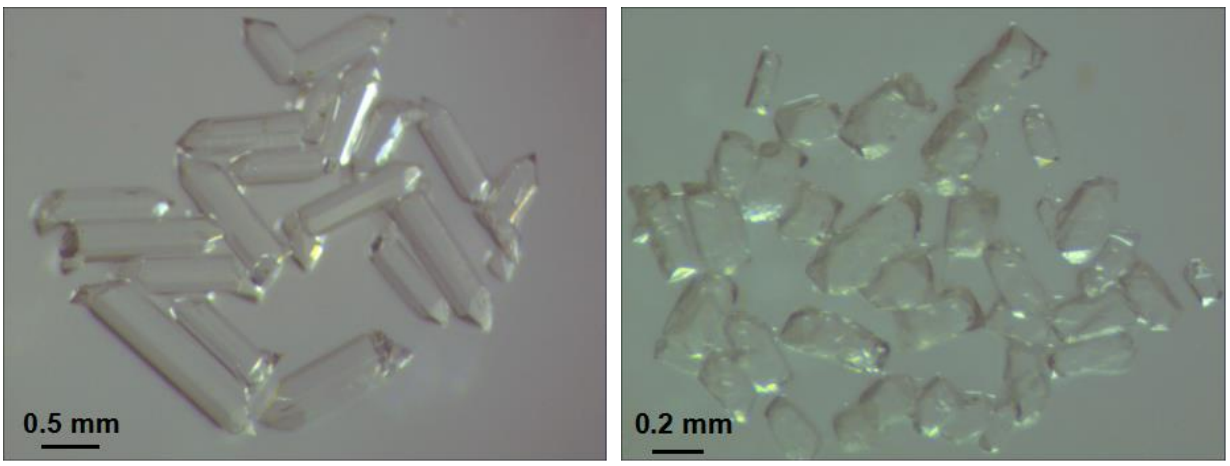
Symmetry codes: a) x - y, - y, - z + 1/3; b) - x + y + 2, - x + 1, z + 1/3; c) -x+2,-x+y+1,-z+2/3; d) y + 1, x - 1, - z + 1; e) - x + y + 1, - x + 1, z - 2/3; f) x, y, z + 1; g) x, y, z - 1; h) - y + 1, x - y, z + 2/3; i) - x + 2, - x + y + 1, - z + 5/3; j) - y + 1, x - y - 1, z - 1/3



SNNU-71 **SNNU-72**



SNNU-73



SNNU-74 **SNNU-75**

Figure S1. The crystal photos of **SNNU-71 -75** under optical microscope**.**

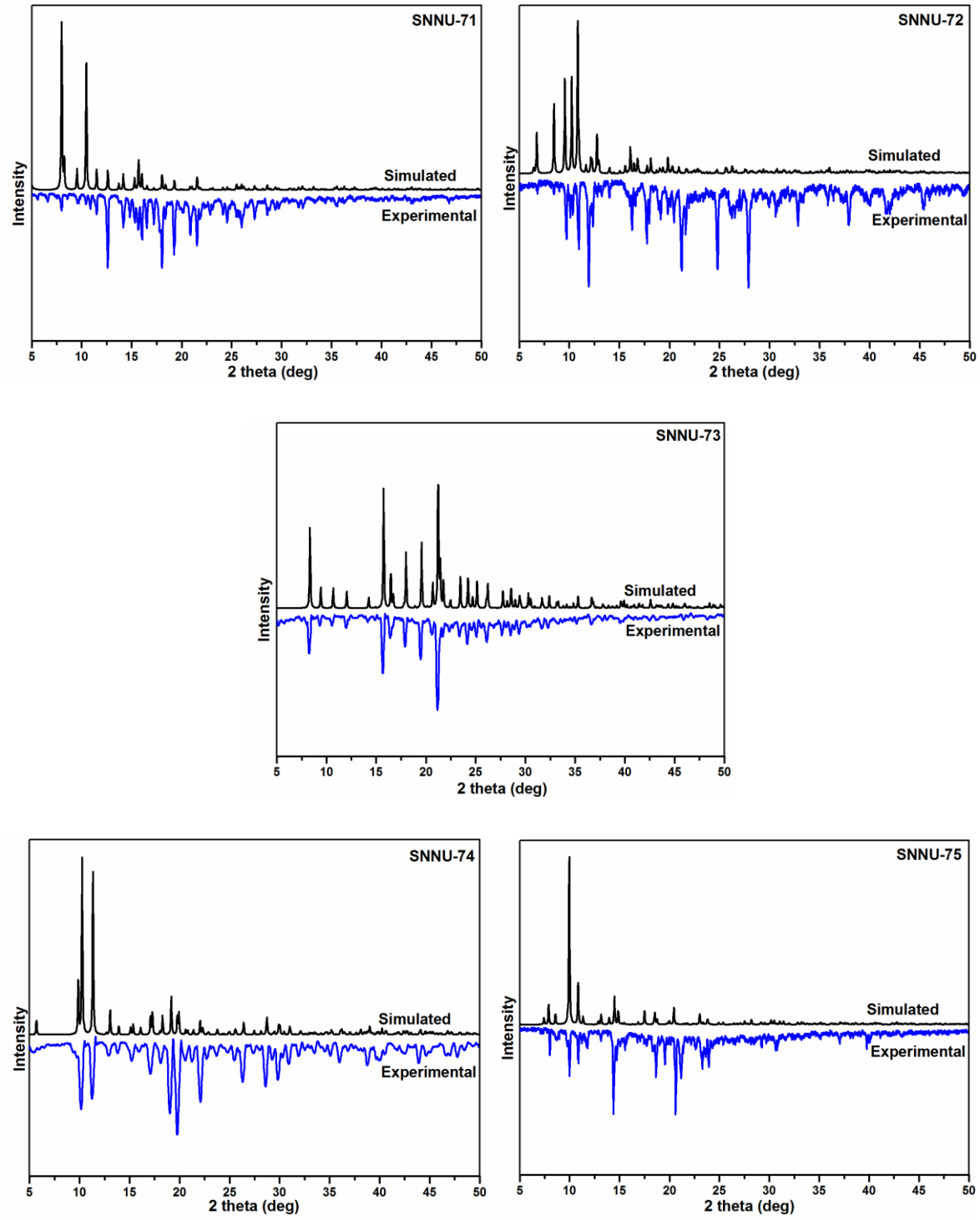


Figure S2. Experimental and simulated PXRD patterns for **SNNU-71-75.**

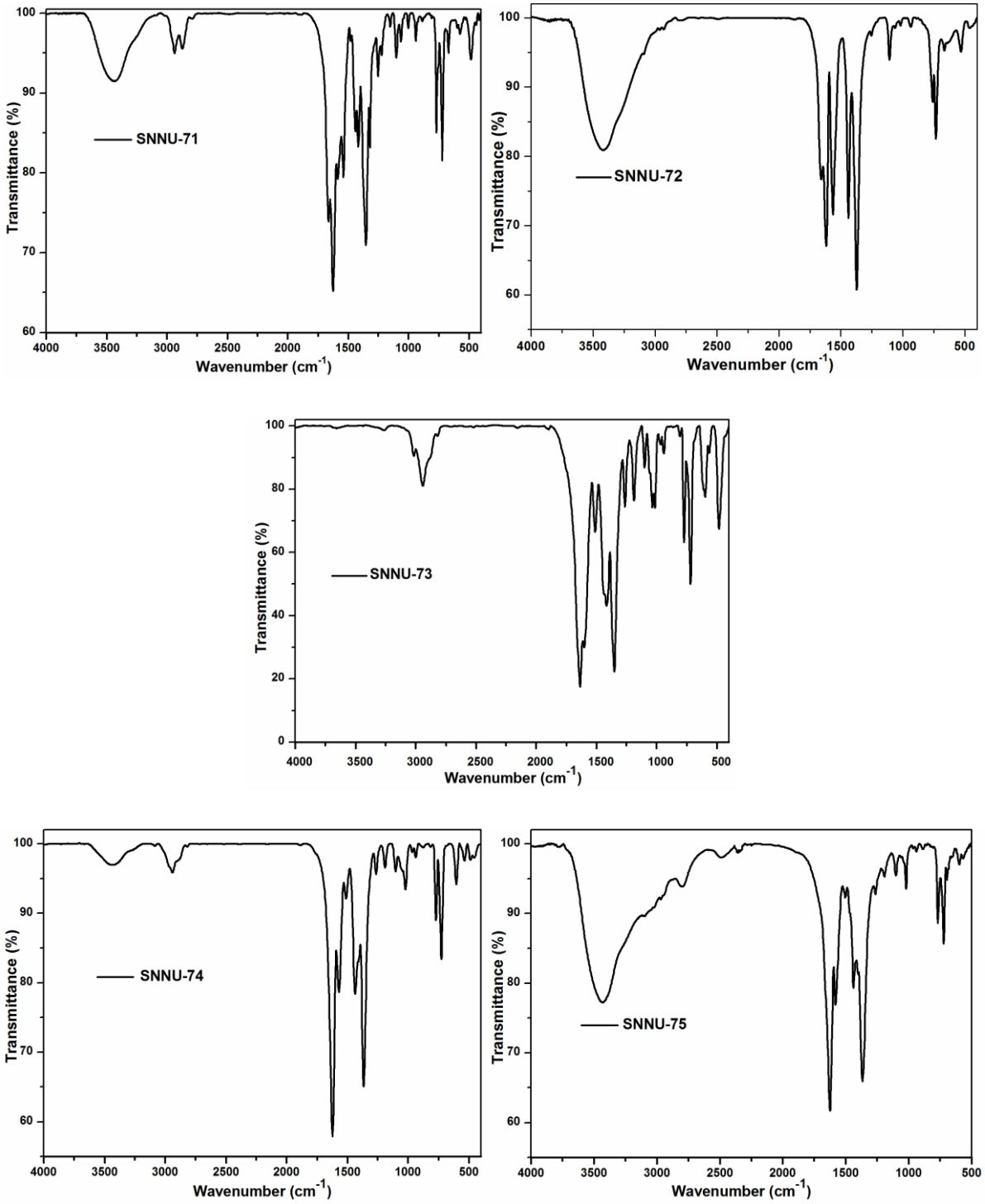


Figure S3. FT-IR spectra for **SNNU-71-75.**

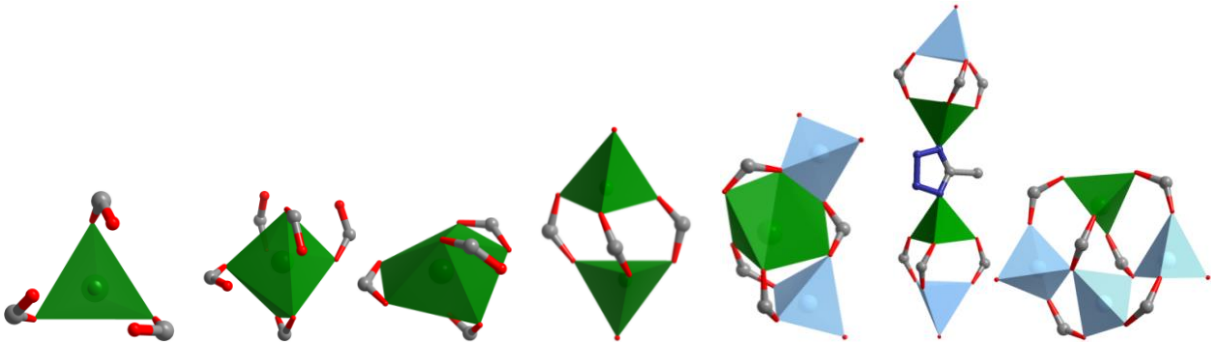


Figure S4. The SBUs for **SNNU-71-75.**

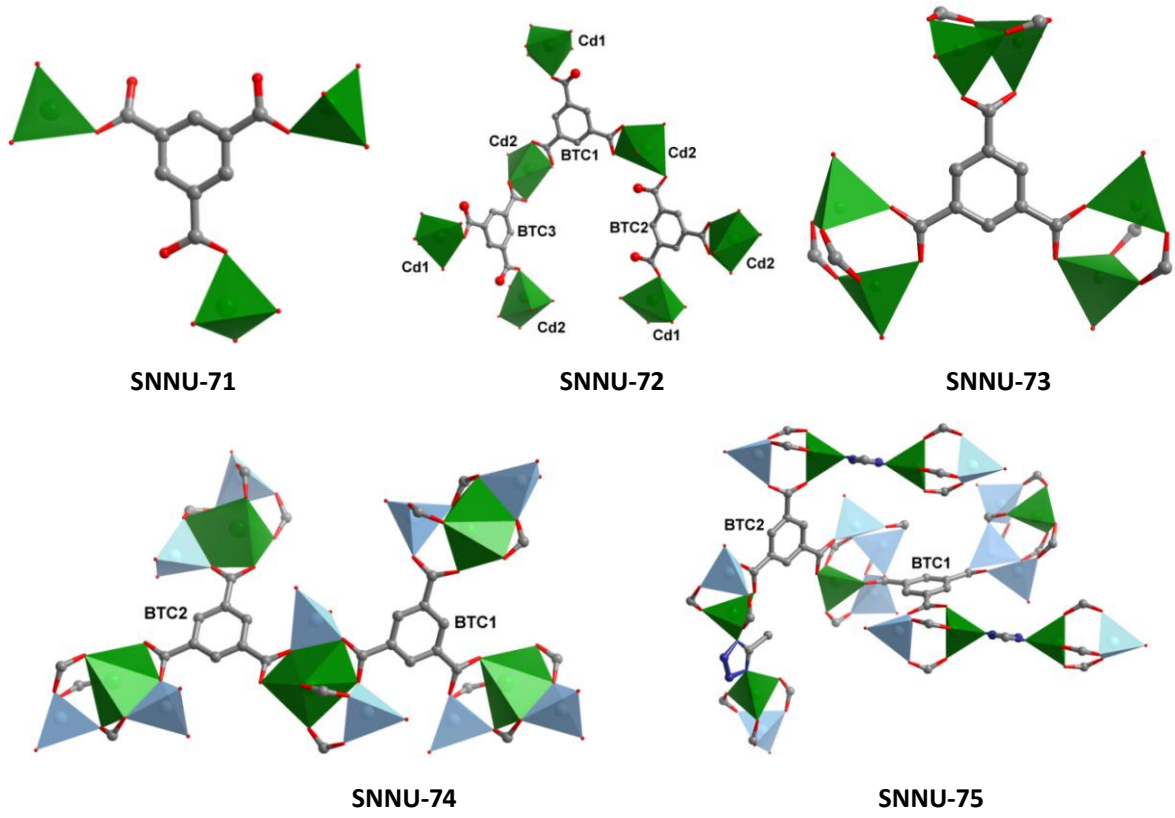
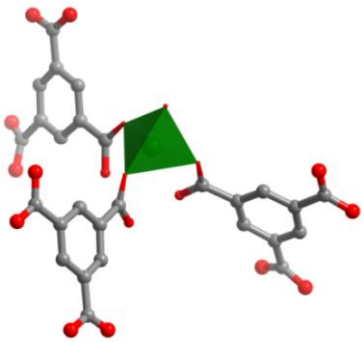
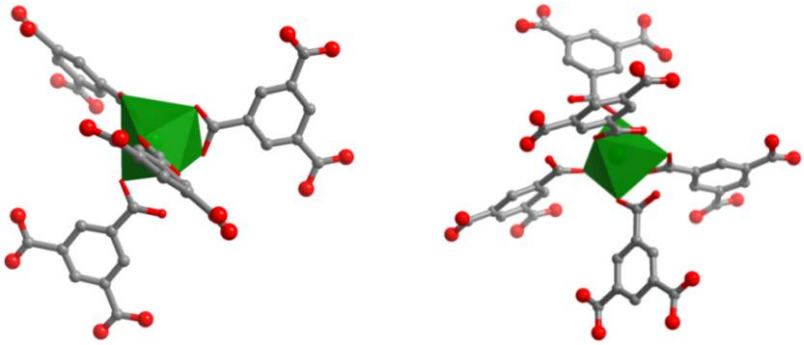


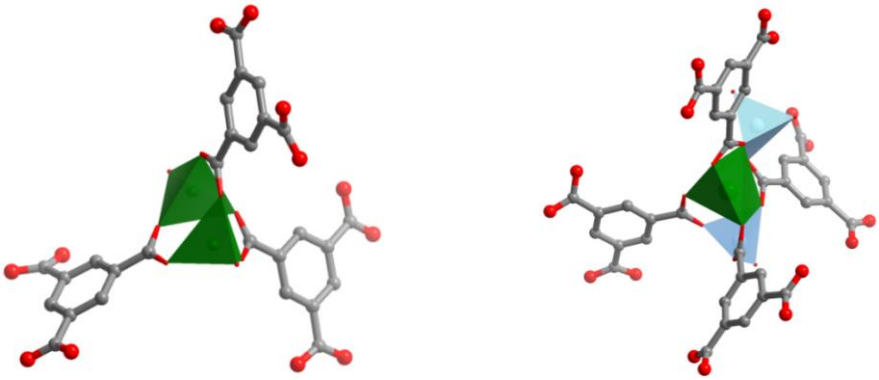
Figure S5. The coordination modes of H_3BTC ligands in **SNNU-71-75.**



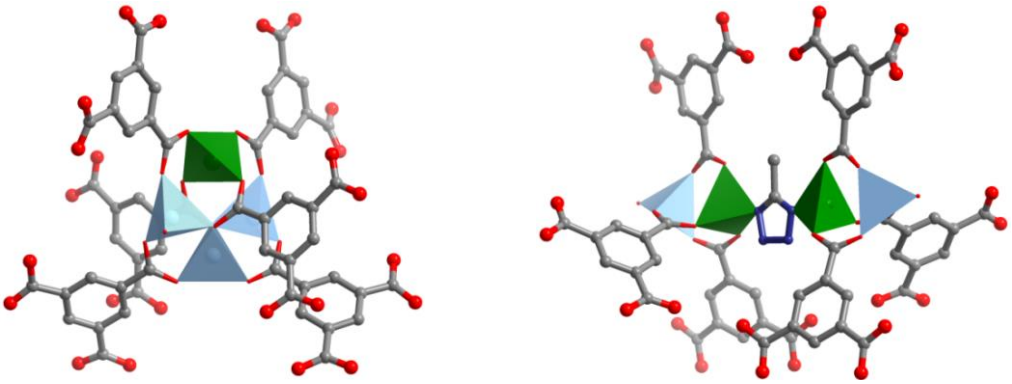
SNNU-71



SNNU-72



SNNU-73 **SNNU-74**



SNNU-75

Figure S6. The distribution of H_3BTC ligands around each SBU in **SNNU-71-75.**

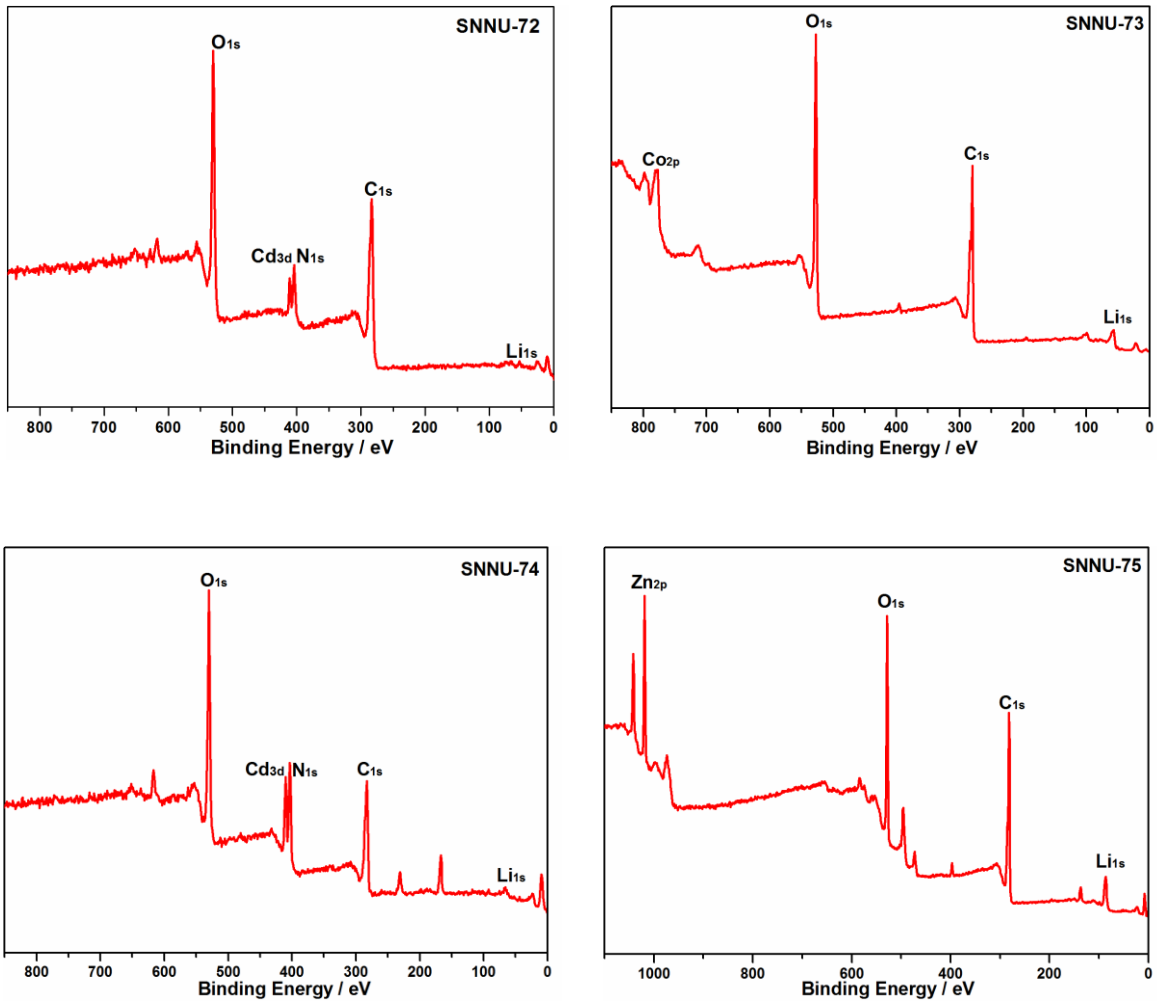


Figure S7. XPS of **SNNU-72-75.**

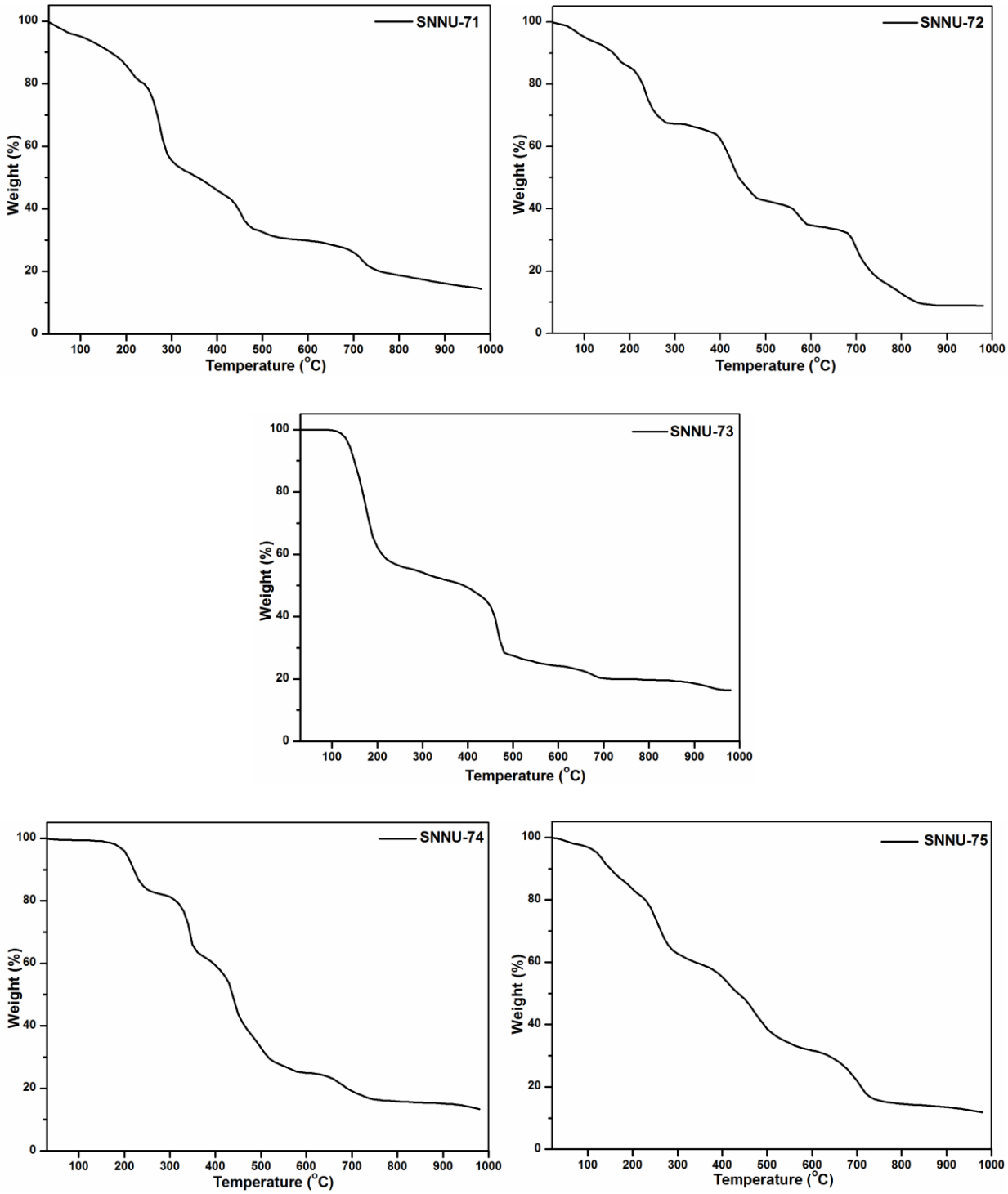
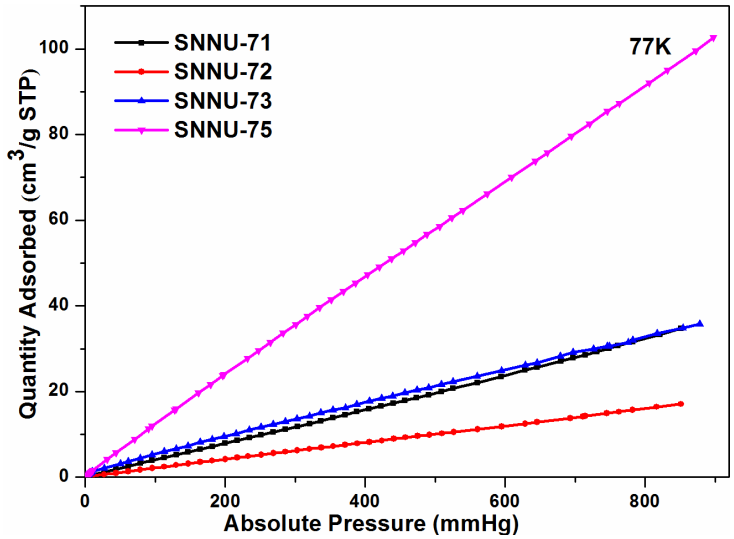
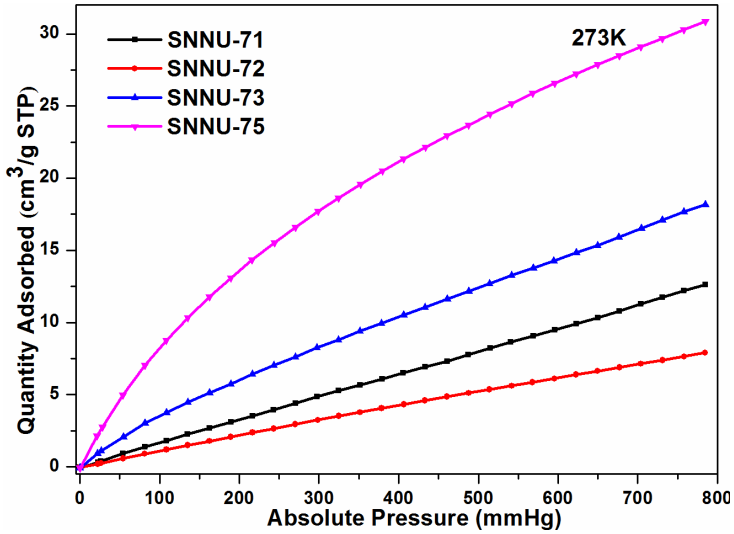


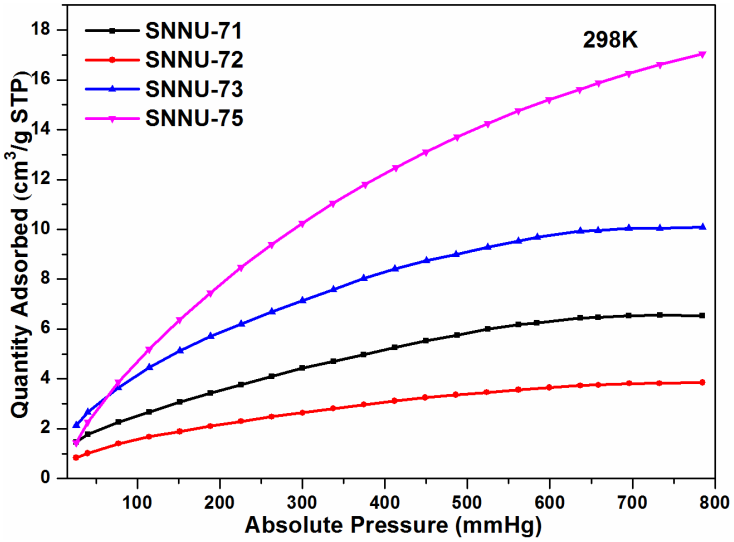
Figure S8. TGA curves for **SNNU-71-75.**



(a)



(b)



(c)

Figure S9. Gas adsorption isotherms of H_2 and CO_2 for compounds **SNNU-71, -72, -73**, and **-75**: (a) H_2 - 77 K; (b) CO_2 - 273 K; (c) CO_2 - 298 K.

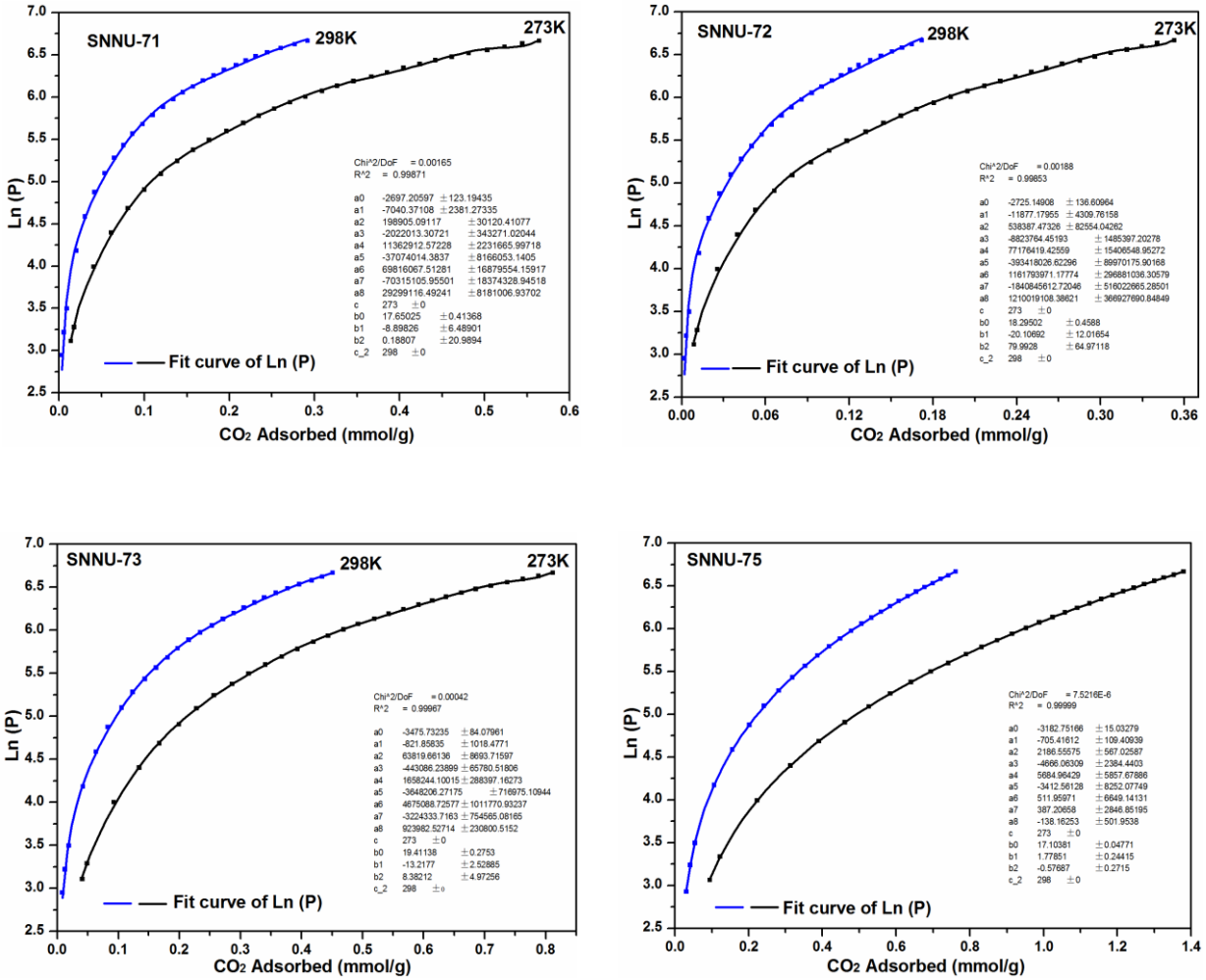


Figure S10. Fitted gas adsorption isotherms of **SNNU-71**, **-72**, **-73**, and **-75** measured at 273 K and 298 K.

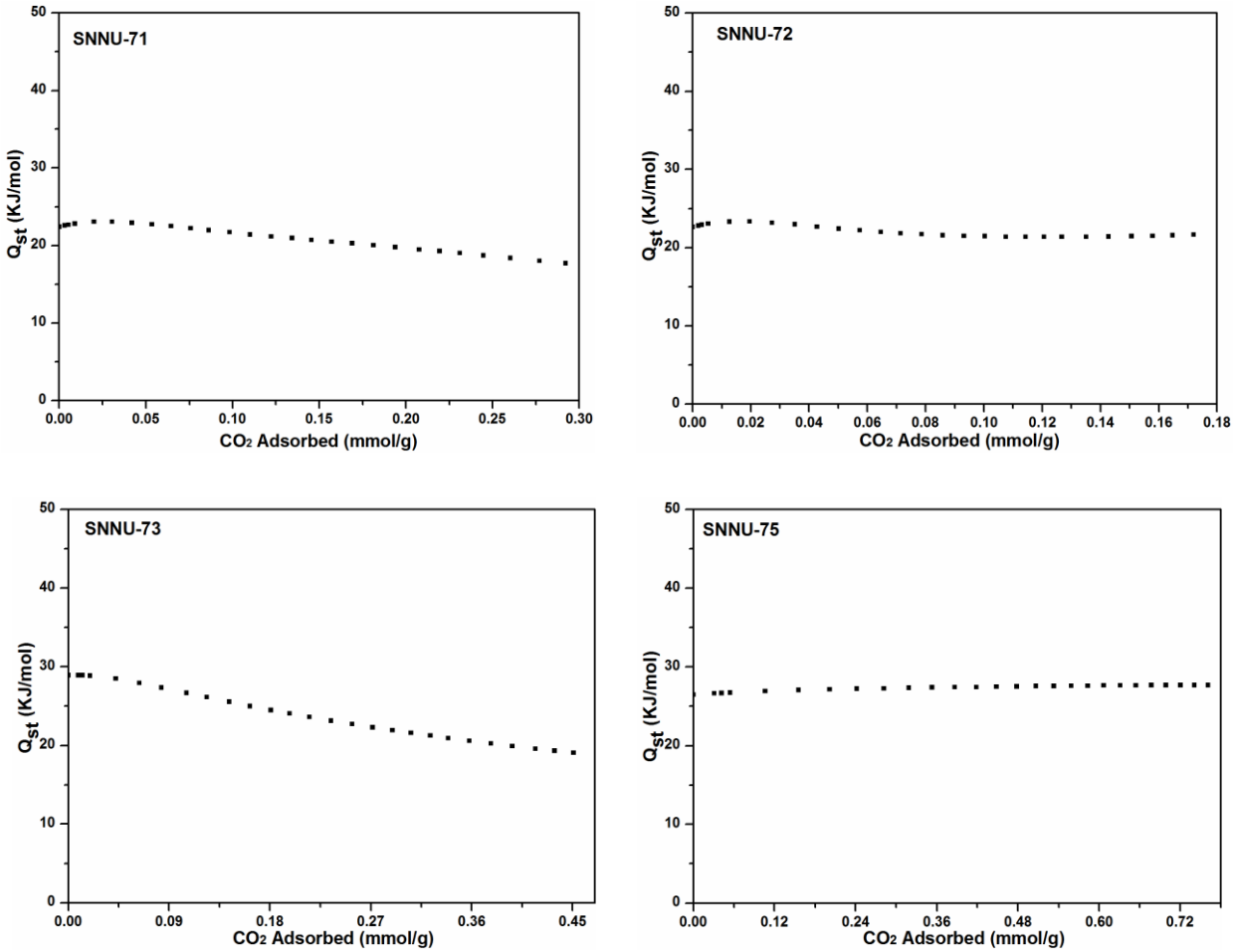


Figure S11. Isosteric heats of adsorption (Q_{st}) for **SNNU-71**, **-72**, **-73**, and **-75.**

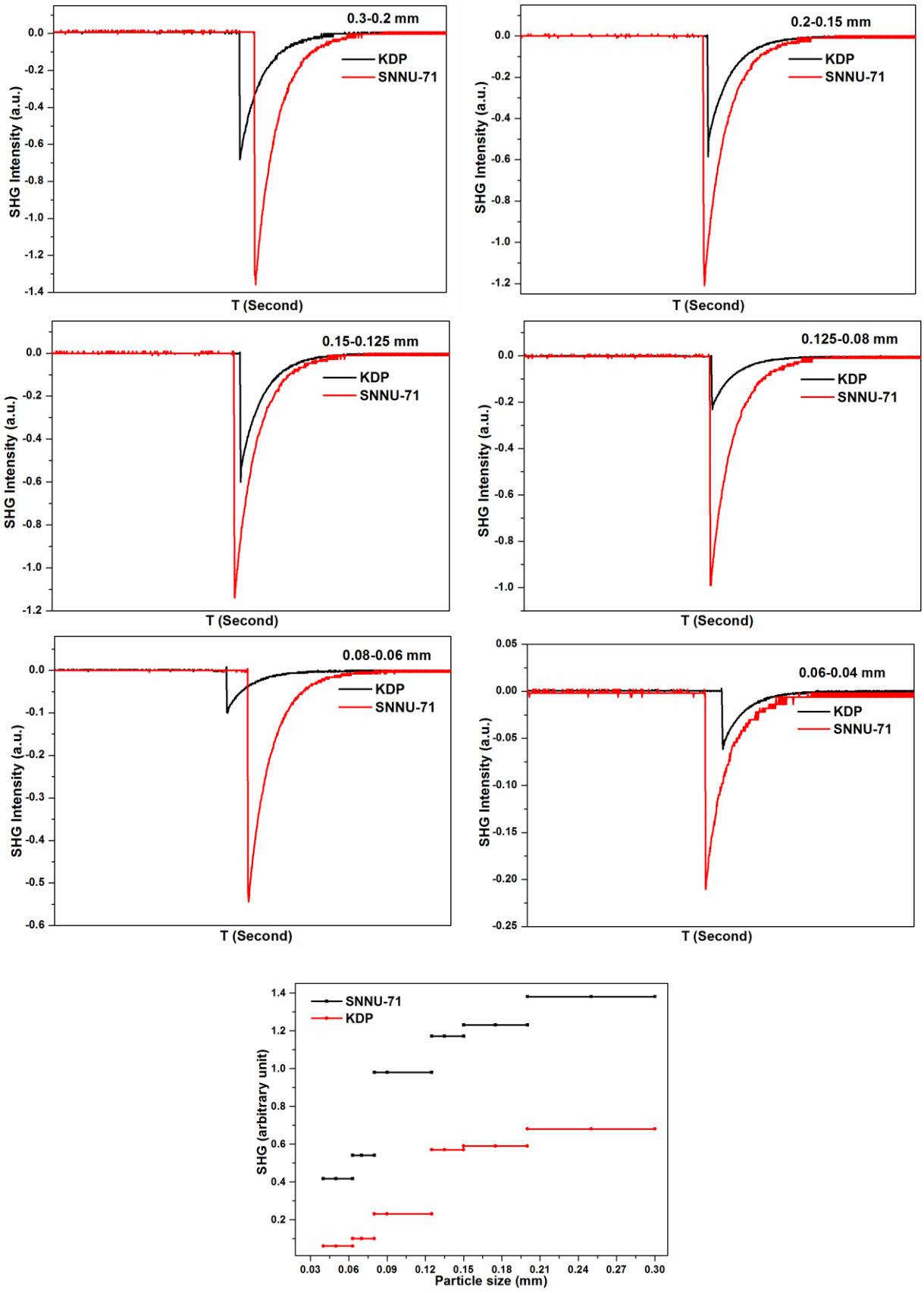


Figure S12. Oscilloscope trace of the SHG signal of **SNNU-71** and KDP at 1064 nm with different in particle size.

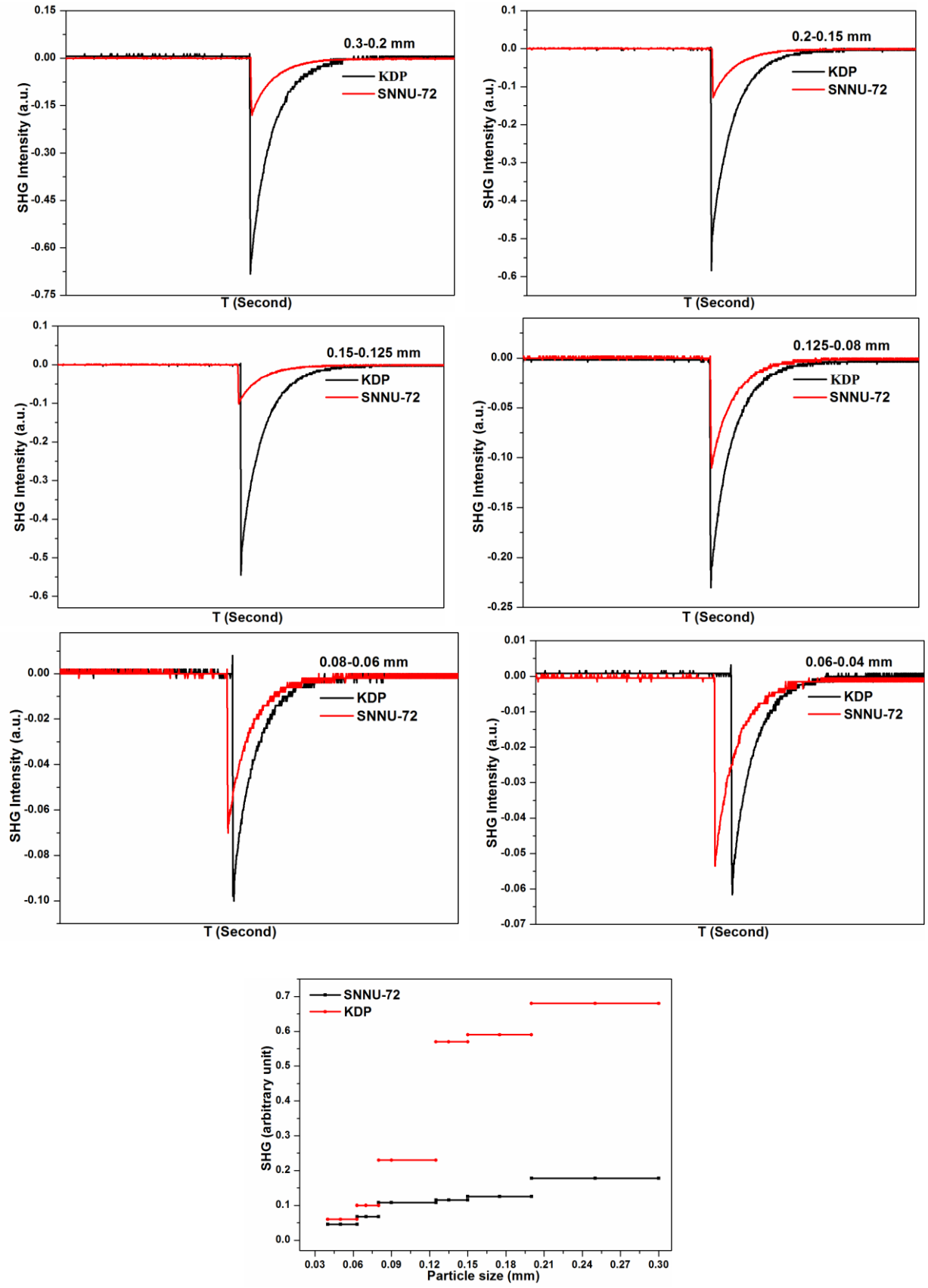


Figure S13. Oscilloscope trace of the SHG signal of **SNNU-72** and KDP at 1064 nm with different in particle size.

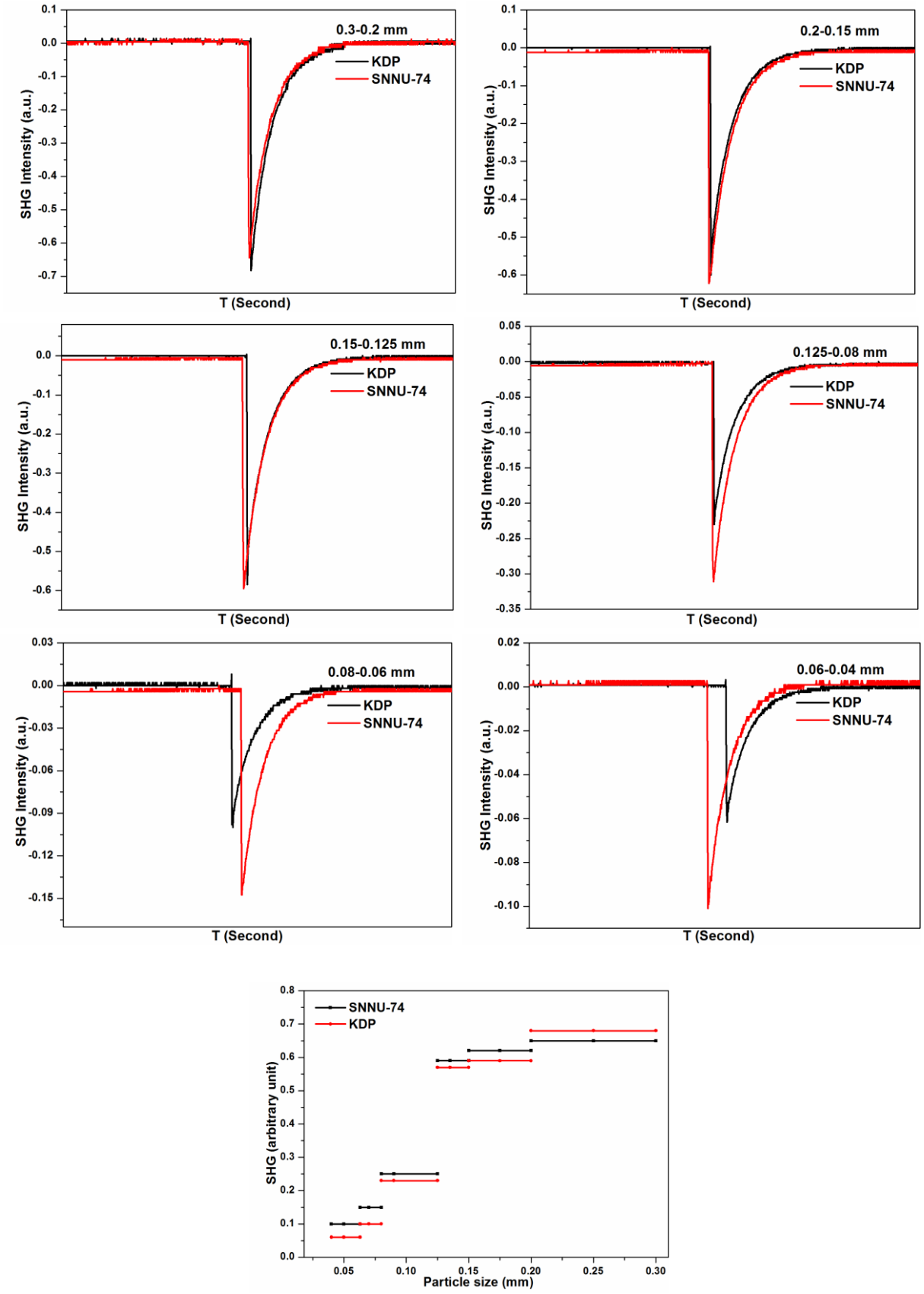


Figure S14. Oscilloscope trace of the SHG signal of **SNNU-74** and KDP at 1064 nm with different in particle size.

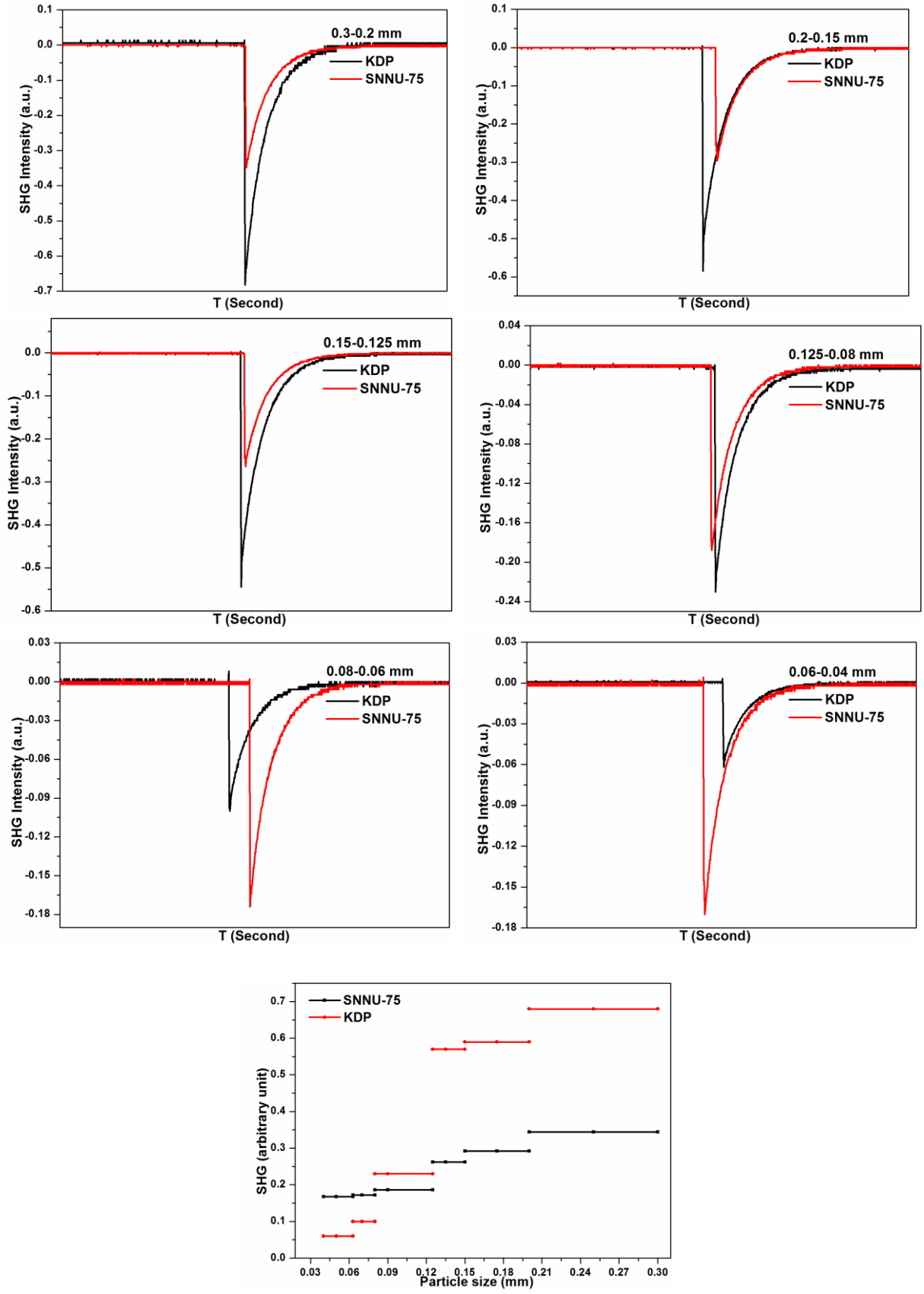


Figure S15. Oscilloscope trace of the SHG signal of **SNNU-75** and KDP at 1064 nm with different in particle size.

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