< Electronic Supporting Information>

Optical limiting effects of 1,10-phenanthroline functionalized heterometallic Sn-Ti oxo clusters with distinct $\pi\cdots\pi$ interactions

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Content

1. Single-crystal X-ray diffraction

Table S1 Crystal data and structure refinement for **TOC-61**, **TOC-62** and **TOC-63**.

Compound	**TOC-61**	**TOC-62**	**TOC-63**
Crystal formula	$C_{130}H_{120}Cl_8N_{18}O_{38}Sn_4Ti_{12}$	$C_{132}H_{132}Cl_8N_{16}O_{38}Sn_4Ti_{12}$	$C_{117}H_{123}Cl_9N_{12}O_{53}Sn_7Ti_{14}$
Formula weight	3875.59	3883.69	4365.75
Temperature/K	293(2)	100.0(3)	100.0(3)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2/n	$P2_1/c$
a/Å	15.5760(3)	18.3926(3)	19.2993(3)
b/Å	16.6681(3)	19.1341(4)	30.2530(5)
c/Å	18.5243(4)	25.1686(5)	30.1640(4)
α/°	105.428(2)	90	90
β/°	100.263(2)	94.912(2)	101.3500(10)
γ/°	108.298(2)	90	90
Volume/Å^3	4217.84(16)	8825.0(3)	17267.2(5)
Z	1	2	4
ρ_{calc}g/cm^3	1.526	1.462	1.679
μ/mm^{-1}	7.435	7.105	10.212
F(000)	1930.0	3880	8576
Crystal size/mm^3	0.002 × 0.001 × 0.001	0.003 × 0.002 × 0.001	0.002 × 0.001 × 0.001
Radiation	micro-focus metaljet (λ = 1.3405)	micro-focus metaljet (λ = 1.3405)	micro-focus metaljet (λ = 1.3405)
2Θ range for data collection/°	4.49 to 120.2	4.014 to 120.35	4.06 to 120.272
Index ranges	-17 ≤ h ≤ 20, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23	-21 ≤ h ≤ 23, -24 ≤ k ≤ 24, -32 ≤ l ≤ 30	-24 ≤ h ≤ 23, -38 ≤ k ≤ 38, -35 ≤ l ≤ 38
Reflections collected	62685	67803	127140
Independent reflections	18752 [R_{int} = 0.0461, R_{sigma} = 0.0547]	19507 [R_{int} = 0.0949, R_{sigma} = 0.0666]	37982 [R_{int} = 0.0928, R_{sigma} = 0.0850]
Data/restraints/parameters	18752/42/961	19507/126/953	37982/2362/1923
Goodness-of-fit on F^2	1.093	1.085	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0636, wR_2 = 0.2110	R_1 = 0.1040, wR_2 = 0.2967	R_1 = 0.0958, wR_2 = 0.2397
Final R indexes [all data]	R_1 = 0.0758, wR_2 = 0.2279	R_1 = 0.1361, wR_2 = 0.3273	R_1 = 0.1369, wR_2 = 0.2688
Largest diff. peak/hole / e Å^{-3}	2.98/-1.26	2.42/-1.39	6.20/-1.59

Table S2 Selected bond lengths (Å) for **TOC-61**.

Ti3-O20	1.821(4)	Ti6-O19	1.831(3)	Ti7-O11	1.828(3)
Ti3-O21	1.832(3)	Ti6-O24	2.091(4)	Ti7-O16[1]	2.111(3)
Ti3-O28	2.124(4)	Ti6-O25	1.806(4)	Ti7-O19	1.833(4)
Ti3-O29	1.819(4)	Ti6-O27	1.853(3)	Ti7-O20	1.814(4)
Ti3-N13	2.232(4)	Ti6-N9	2.288(4)	Ti7-N6	2.232(4)
Ti3-N16	2.234(5)	Ti6-N11	2.254(5)	Ti7-N10	2.249(5)
Ti9-O12	2.033(4)	Ti10-O23	1.796(4)	Ti12-O5	2.041(4)
Ti9-O21	1.904(4)	Ti10-O27	1.848(3)	Ti12-O11[1]	1.886(3)
Ti9-O25	1.802(4)	Ti10-O29[1]	1.853(4)	Ti12-O23	1.813(4)
Ti9-O31	1.845(3)	Ti10-O35	2.077(4)	Ti12-O31	1.840(3)
Ti9-O32	2.072(4)	Ti10-N14	2.258(5)	Ti12-O36	2.062(4)
Ti9-O33	2.091(4)	Ti10-N17	2.298(4)	Ti12-O38	2.084(4)
Sn1-Cl1	2.474(2)	Sn3-Cl3	2.4814(14)		
Sn1-Cl4	2.463(2)	Sn3-O11[1]	2.428(3)		
Sn1-Cl5	2.470(3)	Sn3-O21	2.373(3)		
		Sn3-O31	2.272(3)		

Table S3 Selected bond lengths (Å) for **TOC-62**.

Ti1-O4	1.851(6)	Ti2-O2	2.059(7)	Ti3-O8	1.809(6)
Ti1-O6	1.879(5)	Ti2-O11	1.888(6)	Ti3-O11	1.814(7)
Ti1-O7	2.061(6)	Ti2-O12	1.825(6)	Ti3-O13	2.091(6)
Ti1-O8	1.822(6)	Ti2-O16[1]	1.874(7)	Ti3-O15	1.838(6)
Ti1-O10	2.055(5)	Ti2-O17	2.094(7)	Ti3-N2	2.217(9)
Ti1-O14	2.111(6)	Ti2-O11	2.093(7)	Ti3-N7	2.275(8)
Ti4-O19[1]	1.824(5)	Ti5-O3	2.090(6)	Ti6-O19	1.821(5)
Ti4-O4	1.859(6)	Ti5-O15	1.805(6)	Ti6-O6	1.845(6)
Ti4-O5	2.082(6)	Ti5-O16	1.840(7)	Ti6-O9	2.075(6)
Ti4-O12	1.796(6)	Ti5-O18	1.814(6)	Ti6-O18	1.815(6)
Ti4-N1	2.255(7)	Ti5-N3	2.260(8)	Ti6-N6	2.243(8)
Ti4-N4	2.244(7)	Ti5-N5	2.229(9)	Ti6-N8	2.259(7)
Sn1-Cl1	2.419(4)	Sn3-Cl5	2.412(4)	Sn2-Cl2	2.454(4)
Sn1-O4	2.477(5)	Sn3-O11	2.477(6)	Sn2-Cl3	2.479(3)
Sn1-O41	2.477(5)	Sn3-O11[1]	2.477(6)	Sn2-Cl4	2.450(3)
Sn1-O61	2.462(5)	Sn3-O16	2.469(6)		
Sn1-O6	2.462(5)	Sn3-O16[1]	2.469(6)		

Table S4 Selected bond lengths (Å) for **TOC-63**.

Ti1-O5	1.873(7)	Ti2-O29	1.864(7)	Ti3-O3	2.089(8)
Ti1-O8	2.088(7)	Ti2-O34	1.804(8)	Ti3-O17	1.827(8)
Ti1-O16	2.225(7)	Ti2-O37	2.085(8)	Ti3-O24	1.839(7)
Ti1-O18	1.945(7)	Ti2-O40	1.892(7)	Ti3-O27	2.097(7)
Ti1-O23	1.818(7)	Ti2-O41	2.165(7)	Ti3-O30	2.124(7)
Ti1-O48	1.895(7)	Ti2-O52	2.032(7)	Ti3-O31	1.871(8)
Ti4-O9	1.892(7)	Ti5-O2	1.805(7)	Ti6-O10	2.043(7)
Ti4-O19	2.113(7)	Ti5-O7	1.890(8)	Ti6-O17	1.797(8)
Ti4-O20	1.812(7)	Ti5-O25	2.086(8)	Ti6-O46	1.865(7)
Ti4-O35	2.069(8)	Ti5-O47	1.781(7)	Ti6-O53	1.814(8)
Ti4-O50	2.095(8)	Ti5-N5	2.245(10)	Ti6-N8	2.229(9)
Ti4-O53	1.826(8)	Ti5-N7	2.257(9)	Ti6-N12	2.271(9)
Ti7-O29	1.934(6)	Ti8-O11	1.816(7)	Ti9-O9	1.831(7)
Ti7-O32	1.924(7)	Ti8-O12	1.822(7)	Ti9-O23	1.908(7)
Ti7-O39	2.069(8)	Ti8-O14	2.120(7)	Ti9-O28	2.010(7)
Ti7-O41	2.316(7)	Ti8-O36	1.817(7)	Ti9-O31	1.768(8)
Ti7-O43	1.934(7)	Ti8-N1	2.211(9)	Ti9-N4	2.261(9)
Ti7-O46	1.748(7)	Ti8-N3	2.255(8)	Ti9-N10	2.207(8)
Ti10-O2	1.842(7)	Ti11-O7	1.770(8)	Ti12-O5	1.870(7)
Ti10-O22	2.043(8)	Ti11-O12	1.810(7)	Ti12-O11	1.788(7)
Ti10-O24	1.775(8)	Ti11-O15	2.106(8)	Ti12-O16	2.282(7)
Ti10-O38	2.090(8)	Ti11-O40	1.897(7)	Ti12-O21	2.084(7)
Ti10-O48	1.918(7)	Ti11-N9	2.233(9)	Ti12-O26	2.034(7)
Ti10-O49	2.098(8)	Ti11-N11	2.286(9)	Ti12-O47	1.851(7)
Ti13-O1	1.824(7)	Ti14-O1	1.807(7)	Sn1-Cl4	2.456(3)
Ti13-O20	1.822(7)	Ti14-O4	2.099(8)	Sn1-O29	2.201(7)
Ti13-O32	1.887(7)	Ti14-O34	1.831(7)	Sn1-O40	2.228(6)
Ti13-O33	2.038(8)	Ti14-O36	1.791(7)		
Ti13-O42	2.112(7)	Ti14-N2	2.230(9)		
Ti13-O44	2.150(7)	Ti14-N6	2.267(9)		
Sn2-Cl1	2.476(3)	Sn3-Cl2	2.454(5)	Sn4-O6	2.186(8)
Sn2-O5	2.304(7)	Sn3-Cl3	2.460(5)	Sn4-O32	2.181(7)
Sn2-O9	2.377(6)	Sn3-Cl7	2.529(6)	Sn4-O43	2.092(9)
Sn2-O23	2.422(7)				
Sn5-Cl6	2.464(3)	Sn6-O18	2.102(8)	Sn7-Cl5	2.549(5)
Sn5-Cl8	2.532(4)	Sn6-O45	2.167(8)	Sn7-Cl9	2.470(3)
Sn5-O18	2.058(7)	Sn6-O48	2.171(7)	Sn7-O43	2.069(7)

2. Bond valence sum calculations

Table S5 Bond valence sum values for mental atoms in **TOC-61**.

Ti3	4.244			Ti6	4.156		
Ti3	O20	1.821(4)	0.984	Ti6	O19	1.831(3)	0.958
Ti3	O21	1.832(3)	0.955	Ti6	O24	2.091(4)	0.474
Ti3	O28	2.124(4)	0.434	Ti6	O25	1.806(4)	1.025
Ti3	O29	1.819(4)	0.989	Ti6	O27	1.853(3)	0.902
Ti3	N13	2.232(4)	0.442	Ti6	N9	2.288(4)	0.380
Ti3	N16	2.234(5)	0.440	Ti6	N11	2.254(5)	0.417
Ti7	4.234			Ti9	4.272		
Ti7	O11	1.828(3)	0.965	Ti9	O12	2.033(4)	0.555
Ti7	O16[1]	2.111(3)	0.449	Ti9	O21	1.904(4)	0.786
Ti7	O19	1.833(4)	0.953	Ti9	O25	1.802(4)	1.036
Ti7	O20	1.814(4)	1.003	Ti9	O31	1.845(3)	0.922
Ti7	N6	2.232(4)	0.442	Ti9	O32	2.072(4)	0.499
Ti7	N10	2.249(5)	0.422	Ti9	O33	2.091(4)	0.474
Ti10	4.144			Ti12	4.305		
Ti10	O23	1.796(4)	1.053	Ti12	O5	2.041(4)	0.543
Ti10	O27	1.848(3)	0.915	Ti12	O11[1]	1.886(3)	0.825
Ti10	O29[1]	1.853(4)	0.902	Ti12	O23	1.813(4)	1.005
Ti10	O35	2.077(4)	0.493	Ti12	O31	1.840(3)	0.935
Ti10	N14	2.258(5)	0.412	Ti12	O36	2.062(4)	0.513
Ti10	N17	2.298(4)	0.370	Ti12	O38	2.084(4)	0.483
Sn1	2.558			Sn3	1.810		
Sn1	Cl1	2.474(2)	0.841	Sn3	Cl3	2.4814(14)	0.825
Sn1	Cl4	2.463(2)	0.867	Sn3	O11[1]	2.428(3)	0.267
Sn1	Cl5	2.470(3)	0.850	Sn3	O21	2.373(3)	0.310
				Sn3	O31	2.272(3)	0.408

Table S6 Bond valence sum values for bridging oxygen atoms in **TOC-61**.

O11	2.058	O19	1.910	O20	1.987	O21	2.052	O23	2.058
O25	2.060	O27	1.817	O29	1.892	O31	2.264		

Table S7 Bond valence sum values for mental atoms in **TOC-62**.

Ti1	4.216129			Ti2	4.106201		
Ti1	O4	1.851(6)	0.907286	Ti2	O2	2.059(7)	0.517131
Ti1	O6	1.879(5)	0.84116	Ti2	O11	1.888(6)	0.820947

Ti1	O7	2.061(6)	0.514343	Ti2	O12	1.825(6)	0.973335
Ti1	O8	1.822(6)	0.981259	Ti2	O16[1]	1.874(7)	0.852605
Ti1	O10	2.055(5)	0.522752	Ti2	O17	2.094(7)	0.470455
Ti1	O14	2.111(6)	0.449329	Ti2	O1[1]	2.093(7)	0.471729
Ti3	4.287058			Ti4	4.245954		
Ti3	O8	1.809(6)	1.016348	Ti4	O19[1]	1.824(5)	0.975969
Ti3	O11	1.814(7)	1.002706	Ti4	O4	1.859(6)	0.88788
Ti3	O13	2.091(6)	0.474285	Ti4	O5	2.082(6)	0.485964
Ti3	O15	1.838(6)	0.93973	Ti4	O12	1.796(6)	1.052693
Ti3	N2	2.217(9)	0.460393	Ti4	N1	2.255(7)	0.415456
Ti3	N7	2.275(8)	0.393595	Ti4	N4	2.244(7)	0.427993
Ti5	4.295916			Ti6	4.241419		
Ti5	O3	2.090(6)	0.475569	Ti6	O19	1.821(5)	0.983915
Ti5	O15	1.805(6)	1.027396	Ti6	O6	1.845(6)	0.922119
Ti5	O16	1.840(7)	0.934665	Ti6	O9	2.075(6)	0.495245
Ti5	O18	1.814(6)	1.002706	Ti6	O18	1.815(6)	1
Ti5	N3	2.260(8)	0.40988	Ti6	N6	2.243(8)	0.429151
Ti5	N5	2.229(9)	0.4457	Ti6	N8	2.259(7)	0.410989
Sn1	1.932367			Sn3	1.941863		
Sn1	Cl1	2.419(4)	0.975969	Sn3	Cl5	2.412(4)	0.994609
Sn1	O4	2.477(5)	0.234254	Sn3	O11	2.477(6)	0.234254
Sn1	O4[1]	2.477(5)	0.234254	Sn3	O11[1]	2.477(6)	0.234254
Sn1	O6[1]	2.462(5)	0.243945	Sn3	O16	2.469(6)	0.239374
Sn1	O6	2.462(5)	0.243945	Sn3	O16[1]	2.469(6)	0.239374
Sn2	2.61528						
Sn2	Cl2	2.454(4)	0.88788				
Sn2	Cl3	2.479(3)	0.82987				
Sn2	Cl4	2.450(3)	0.897531				

Table S8 Bond valence sum values for bridging oxygen atoms in **TOC-62.**

O4	2.029	O6	2.007	O8	1.995	O11	2.060	O12	2.026
O15	1.967	O16	2.026	O18	2.005	O19	1.960		

Table S9 Bond valence sum values for mental atoms in **TOC-63**.

Ti1	4.164			Ti2	4.145		
Ti1	O5	1.873(7)	0.855	Ti2	O29	1.864(7)	0.876
Ti1	O8	2.088(7)	0.478	Ti2	O34	1.804(8)	1.030
Ti1	O16	2.225(7)	0.330	Ti2	O37	2.085(8)	0.482
Ti1	O18	1.945(7)	0.704	Ti2	O40	1.892(7)	0.812

Ti1	O23	1.818(7)	0.992	Ti2	O41	2.165(7)	0.388
Ti1	O48	1.895(7)	0.806	Ti2	O52	2.032(7)	0.556
Ti3	4.142			Ti4	4.210		
Ti3	O3	2.089(8)	0.477	Ti4	O9	1.892(7)	0.812
Ti3	O17	1.827(8)	0.968	Ti4	O19	2.113(7)	0.447
Ti3	O24	1.839(7)	0.937	Ti4	O20	1.812(7)	1.008
Ti3	O27	2.097(7)	0.467	Ti4	O35	2.069(8)	0.503
Ti3	O30	2.124(7)	0.435	Ti4	O50	2.095(8)	0.469
Ti3	O31	1.871(8)	0.860	Ti4	O53	1.826(8)	0.971
Ti5	4.261			Ti6	4.310		
Ti5	O2	1.805(7)	1.027	Ti6	O10	2.043(7)	0.540
Ti5	O7	1.890(8)	0.817	Ti6	O17	1.797(8)	1.050
Ti5	O25	2.086(8)	0.481	Ti6	O46	1.865(7)	0.874
Ti5	O47	1.781(7)	1.096	Ti6	O53	1.814(8)	1.003
Ti5	N5	2.245(10)	0.427	Ti6	N8	2.229(9)	0.446
Ti5	N7	2.257(9)	0.413	Ti6	N12	2.271(9)	0.398
Ti7	4.155			Ti8	4.295		
Ti7	O29	1.934(6)	0.725	Ti8	O11	1.816(7)	0.997
Ti7	O32	1.924(7)	0.745	Ti8	O12	1.822(7)	0.981
Ti7	O39	2.069(8)	0.503	Ti8	O14	2.120(7)	0.439
Ti7	O41	2.316(7)	0.258	Ti8	O36	1.817(7)	0.995
Ti7	O43	1.934(7)	0.725	Ti8	N1	2.211(9)	0.468
Ti7	O46	1.748(7)	1.199	Ti8	N3	2.255(8)	0.415
Ti9	4.343			Ti10	4.282		
Ti9	O9	1.831(7)	0.958	Ti10	O2	1.842(7)	0.930
Ti9	O23	1.908(7)	0.778	Ti10	O22	2.043(8)	0.540
Ti9	O28	2.010(7)	0.590	Ti10	O24	1.775(8)	1.114
Ti9	O31	1.768(8)	1.135	Ti10	O38	2.090(8)	0.476
Ti9	N4	2.261(9)	0.409	Ti10	O48	1.918(7)	0.757
Ti9	N10	2.207(8)	0.473	Ti10	O49	2.098(8)	0.465
Ti11	4.223			Ti12	4.165		
Ti11	O7	1.770(8)	1.129	Ti12	O5	1.870(7)	0.862
Ti11	O12	1.810(7)	1.014	Ti12	O11	1.788(7)	1.076
Ti11	O15	2.106(8)	0.455	Ti12	O16	2.282(7)	0.283
Ti11	O40	1.897(7)	0.801	Ti12	O21	2.084(7)	0.483
Ti11	N9	2.233(9)	0.441	Ti12	O26	2.034(7)	0.553
Ti11	N11	2.286(9)	0.382	Ti12	O47	1.851(7)	0.907
Ti13	4.180			Ti14	4.357		
Ti13	O1	1.824(7)	0.976	Ti14	O1	1.807(7)	1.021

Ti13	O20	1.822(7)	0.981	Ti14	O4	2.099(8)	0.464
Ti13	O32	1.887(7)	0.823	Ti14	O34	1.831(7)	0.958
Ti13	O33	2.038(8)	0.547	Ti14	O36	1.791(7)	1.067
Ti13	O42	2.112(7)	0.448	Ti14	N2	2.230(9)	0.444
Ti13	O44	2.150(7)	0.404	Ti14	N6	2.267(9)	0.402
Sn1	1.836			Sn2	1.789262		
Sn1	Cl4	2.456(3)	0.883	Sn2	Cl1	2.476(3)	0.837
Sn1	O29	2.201(7)	0.494	Sn2	O5	2.304(7)	0.374
Sn1	O40	2.228(6)	0.459	Sn2	O9	2.377(6)	0.307
				Sn2	O23	2.422(7)	0.272
Sn3	2.486			Sn4	1.699		
Sn3	Cl2	2.454(5)	0.888	Sn4	O6	2.186(8)	0.514
Sn3	Cl3	2.460(5)	0.874	Sn4	O32	2.181(7)	0.521
Sn3	Cl7	2.529(6)	0.725	Sn4	O43	2.092(9)	0.663
Sn5	2.310			Sn6	1.722		
Sn5	Cl6	2.464(3)	0.864	Sn6	O18	2.102(8)	0.645
Sn5	Cl8	2.532(4)	0.719	Sn6	O45	2.167(8)	0.541
Sn5	O18	2.058(7)	0.727	Sn6	O48	2.171(7)	0.536
Sn7	2.243						
Sn7	Cl5	2.549(5)	0.687				
Sn7	Cl9	2.470(3)	0.850				
Sn7	O43	2.069(7)	0.706				

Table S10 Bond valence sum values for bridging oxygen atoms in **TOC-63.**

O1	1.998	O2	1.957	O5	2.091	O7	1.946	O9	2.077
O11	2.073	O12	1.995	O17	2.018	O18	1.891	O20	1.989
O23	2.041	O24	2.051	O29	2.095	O31	1.995	O32	2.089
O34	1.988	O36	2.062	O40	2.072	O43	1.891	O46	2.072
O47	2.004	O48	2.098	O53	1.973				

3. Additional structural pictures

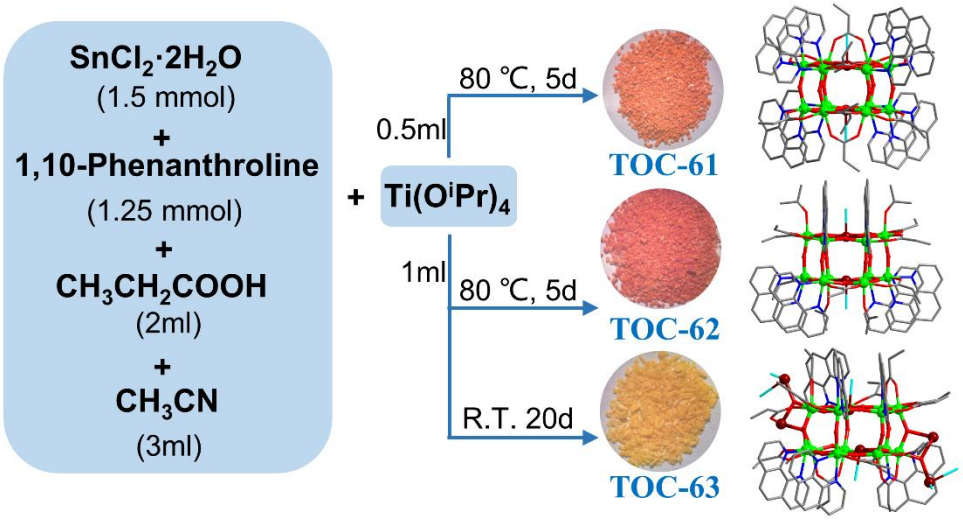

Figure S1 Synthetic route to three compounds.

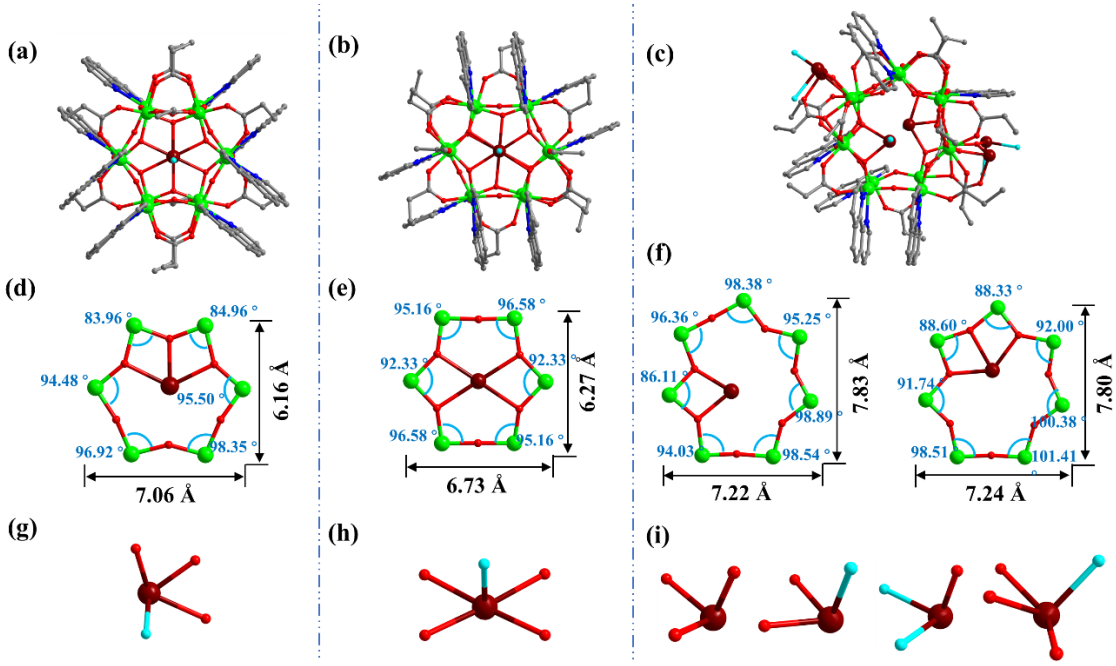

Figure S2 Top views of the total molecular structure of **TOC-61** (a), **TOC-62** (b), **TOC-63** (c). Detail drawing of **TOC-61** (d), **TOC-62** (e), **TOC-63** (f). The Coordination environment diagram of Sn^{2+} in **TOC-61** (g), **TOC-62** (h), **TOC-63** (i).

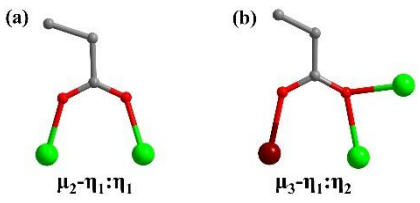

Figure S3 The coordination modes of propionic acid ligand in **TOC-63**.

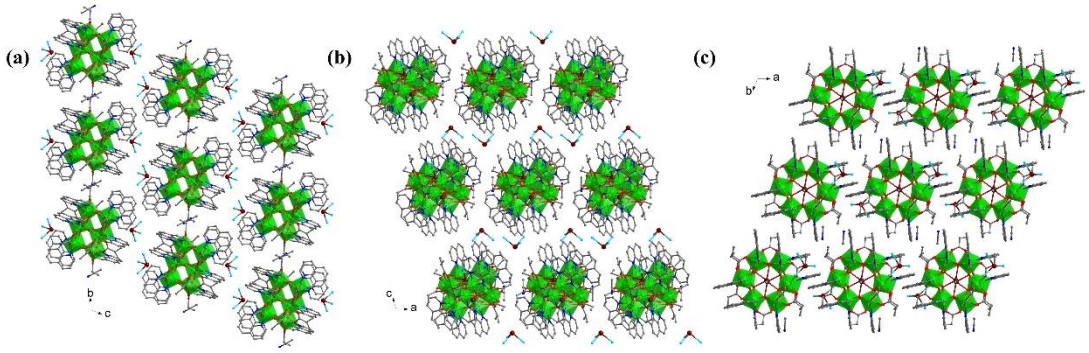

Figure S4 Packing diagrams of **TOC-61** in the view of (a) a-axis, (b) b-axis and (c) c-axis.

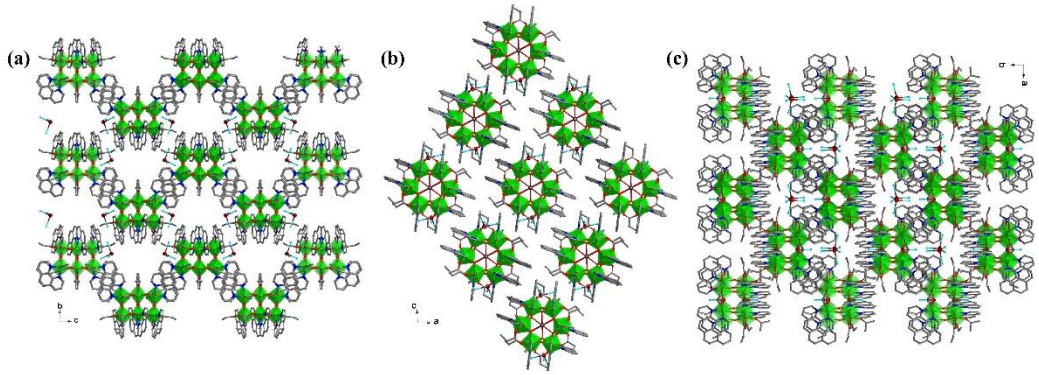

Figure S5 Packing diagrams of **TOC-62** in the view of (a) a-axis, (b) b-axis and (c) c-axis.

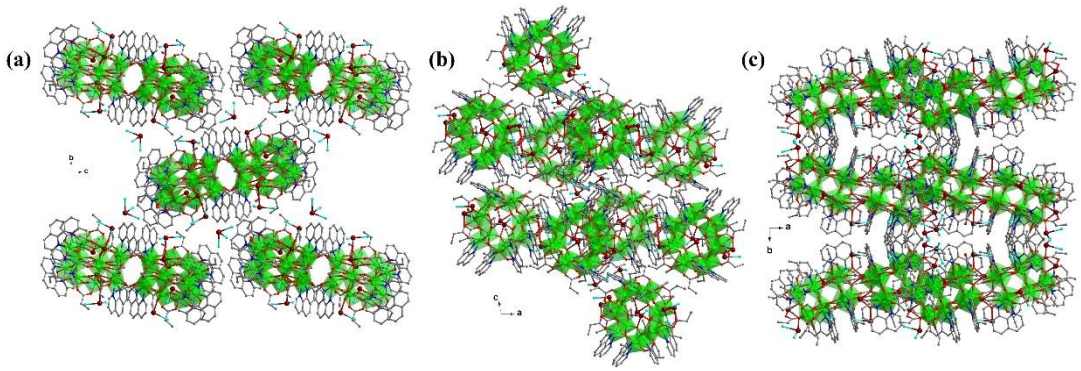

Figure S6 Packing diagrams of **TOC-63** in the view of (a) a-axis, (b) b-axis and (c) c-axis.

4. Powder-XRD patterns

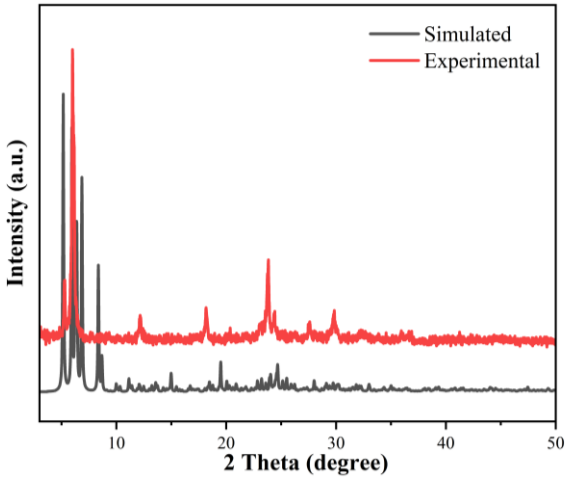

Figure S7 Simulated and experimental PXRD patterns of **TOC-61**.

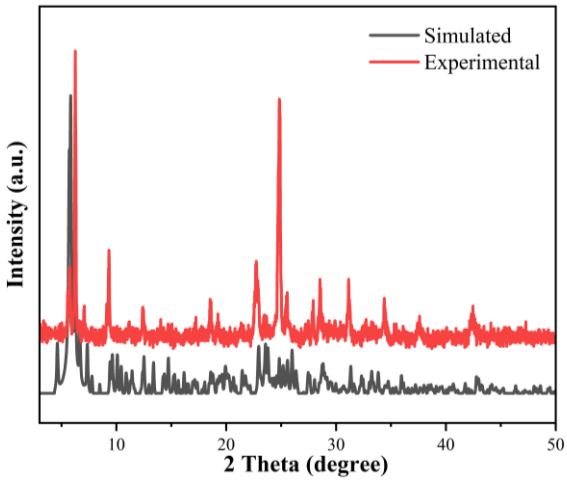

Figure S8 Simulated and experimental PXRD patterns of **TOC-62**.

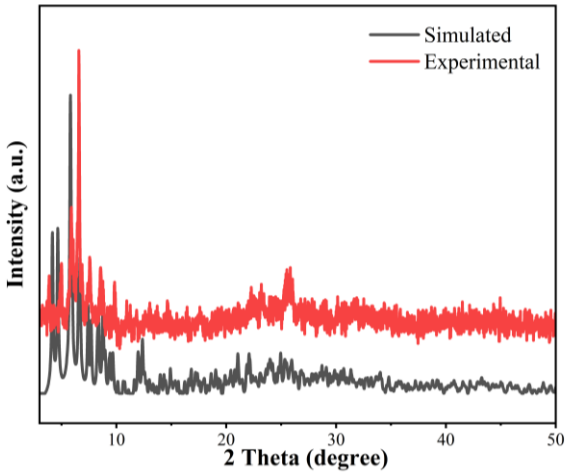

Figure S9 Simulated and experimental PXRD patterns of **TOC-63**.

5. The energy dispersive X-ray spectroscopy (EDS) spectra

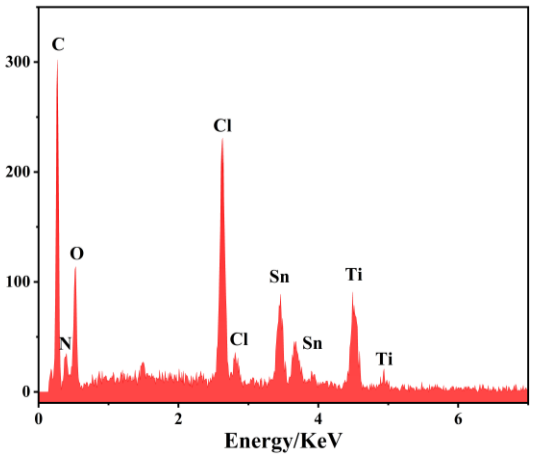

Figure S10 The EDS spectrum of **TOC-61**.

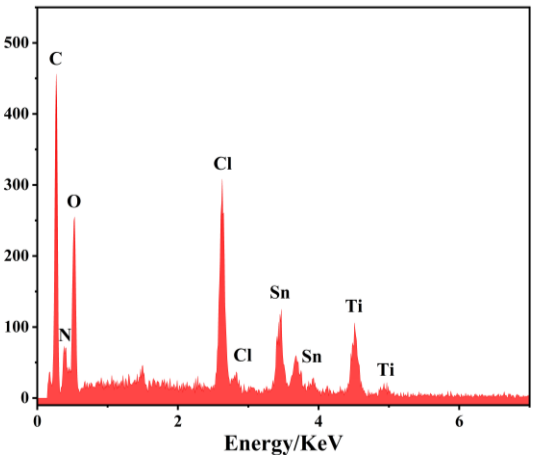

Figure S11 The EDS spectrum of **TOC-62**.

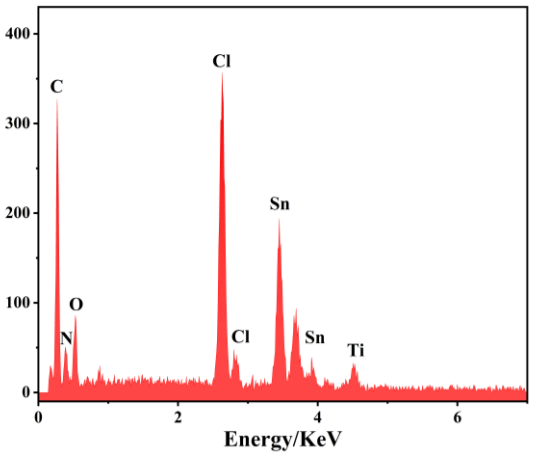

Figure S12 The EDS spectrum of **TOC-63**.

6. Thermogravimetrical analysis (TG)

By analyzing the TG curves of **TOC-61** to **TOC-63**, it was observed that the skeleton of the three compounds remained relatively stable until ~200 ℃. Beyond this temperature, ligand detachment and structure decomposition occurred.

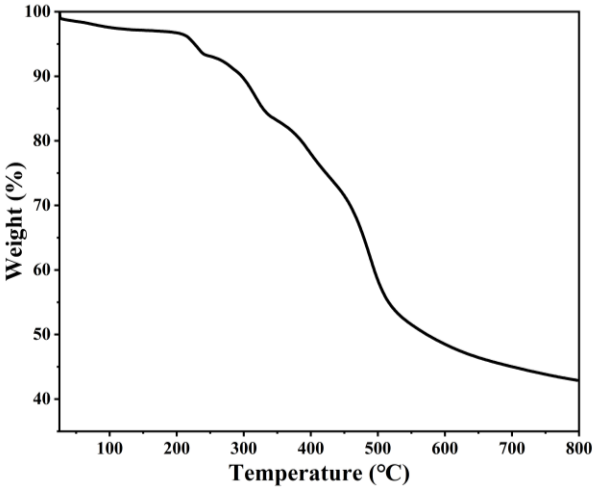

Figure S13 TG curve of **TOC-61** in N_2 atmosphere.

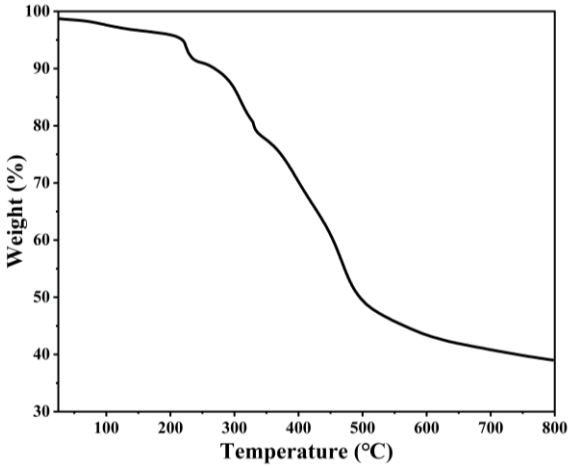

Figure S14 TG curve of **TOC-62** in N_2 atmosphere.

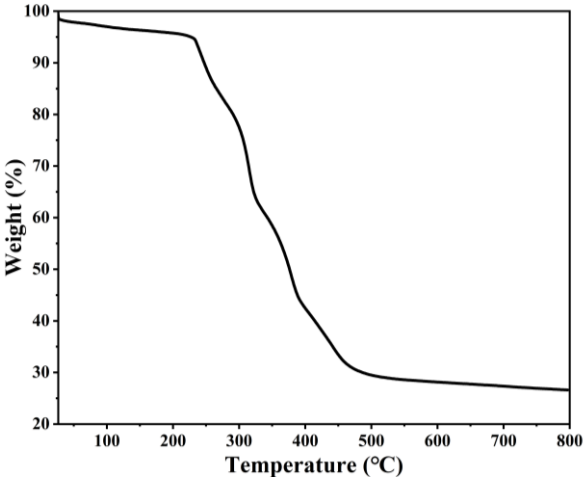

Figure S15 TG curve of **TOC-63** in N_2 atmosphere.

7. IR spectra

The band around 3300~2800 cm^{-1} is attributed to v(C-H). The incorporation of 1,10-phenanthroline is supported by the C-H vibration at 3100~3010 cm^{-1}, and the absorption peak in the range of 1750~1410 cm^{-1} belongs to the stretching vibration of C=O on the carboxyl group. The absorption peak below 1000 cm^{-1} is associated with v(M-O-M).

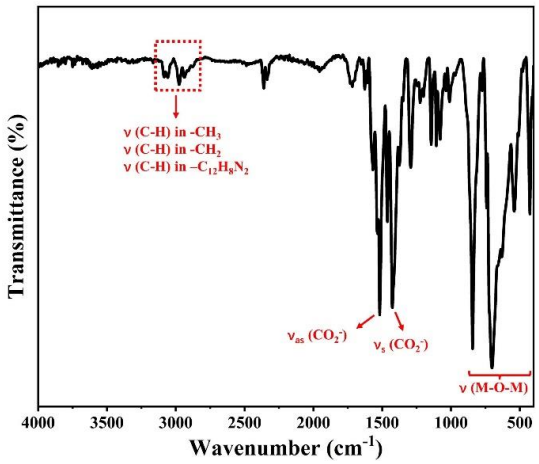

Figure S16 FT-IR spectrum of **TOC-61**.

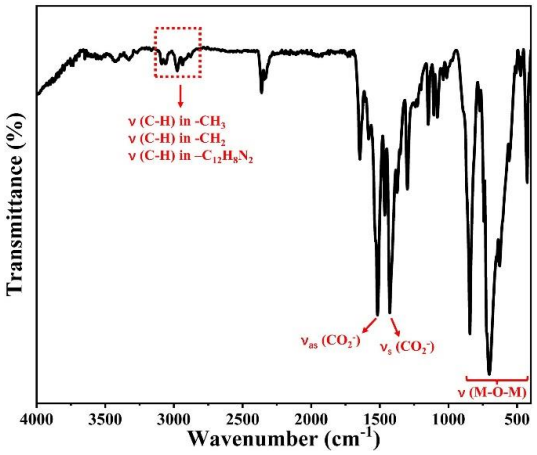

Figure S17 FT-IR spectrum of **TOC-62**.

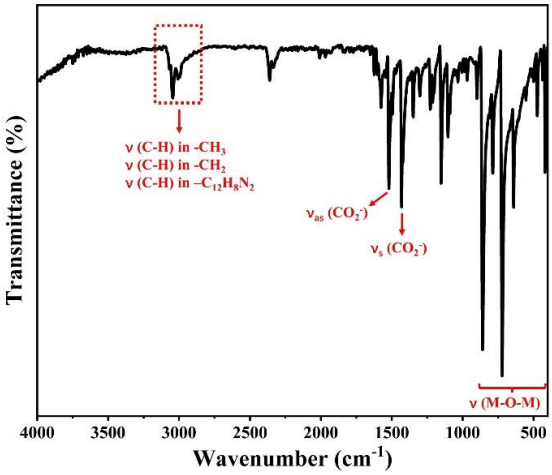

Figure S18 FT-IR spectrum of **TOC-63**.

8. XPS spectra

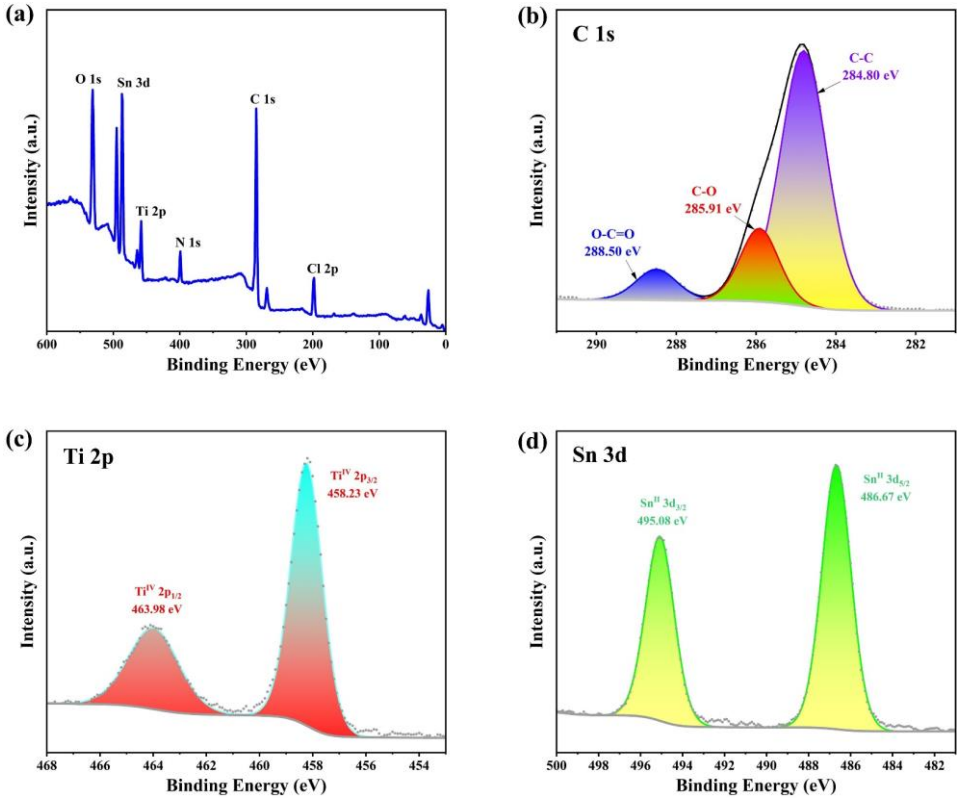

Figure S19 XPS spectra of **TOC-61**.

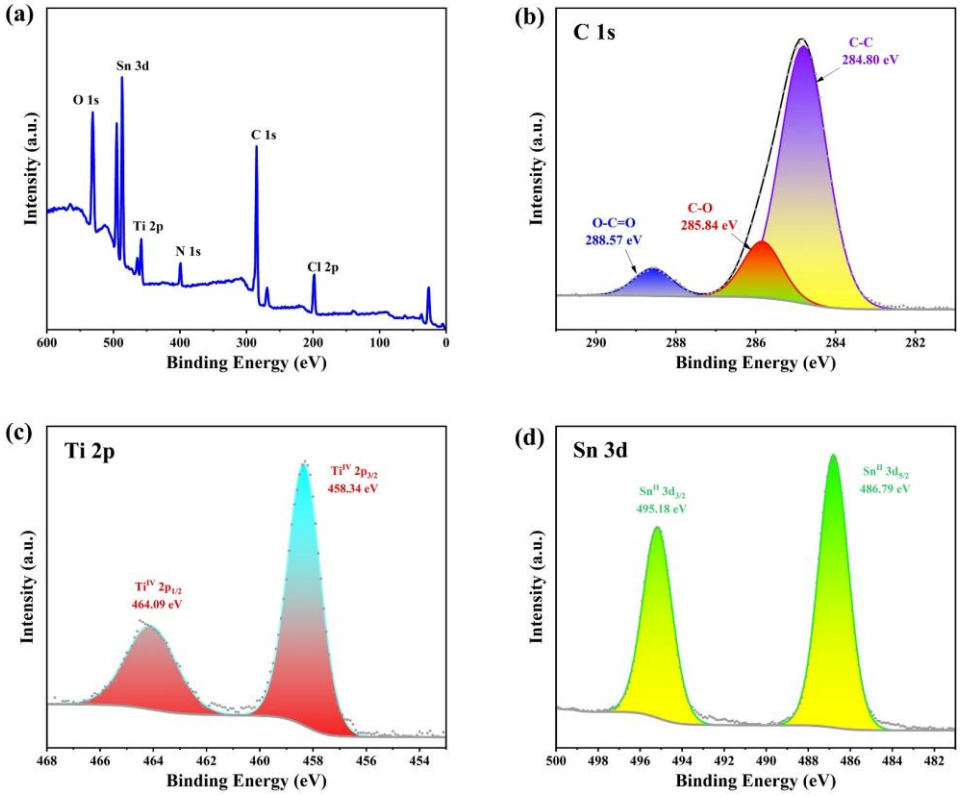

Figure S20 XPS spectra of **TOC-62**.

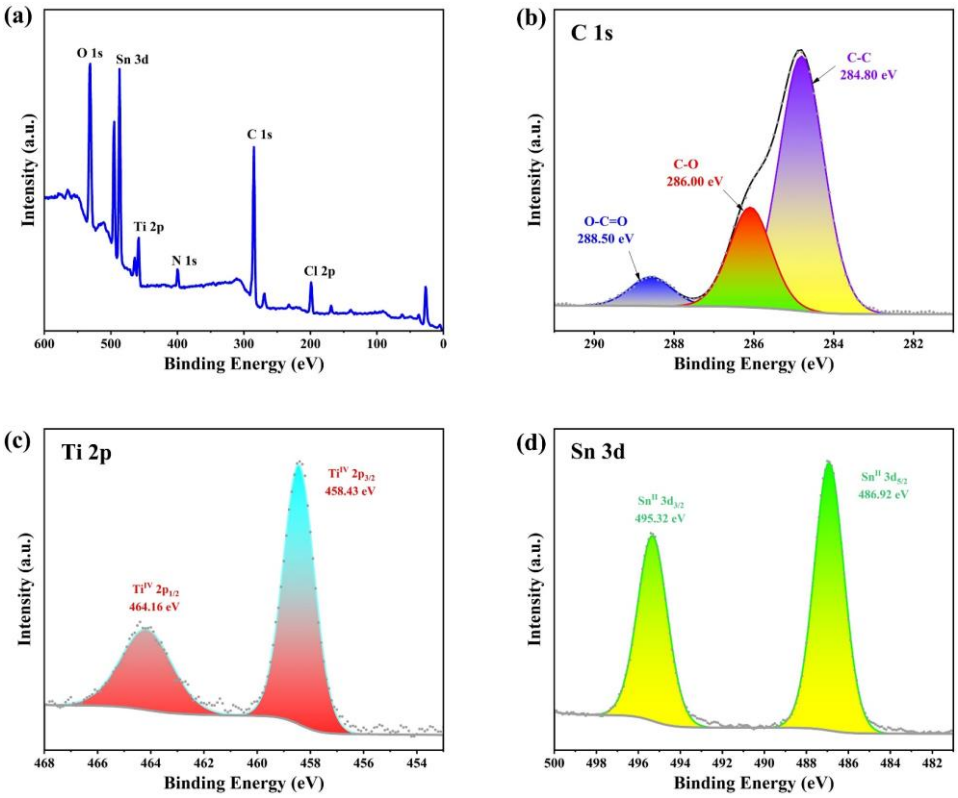

Figure S21 XPS spectra of **TOC-63**.

9. The NLO Property

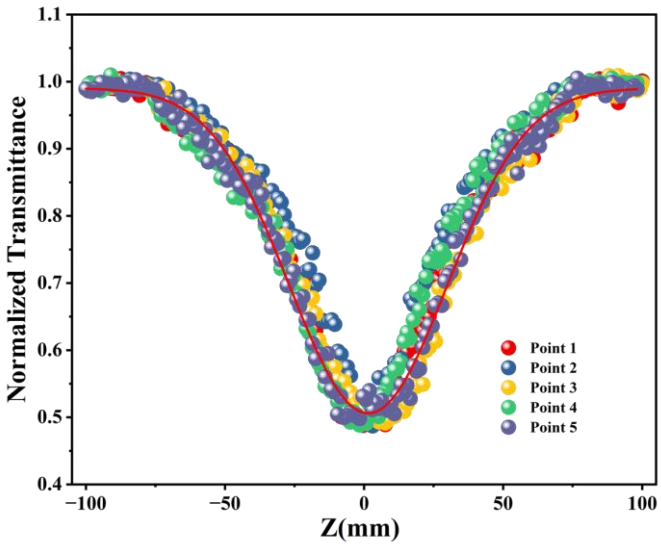

Figure S22 The open-aperture Z-scan results at 532 nm for **TOC-61** thin film: the same thin film is tested at different points.

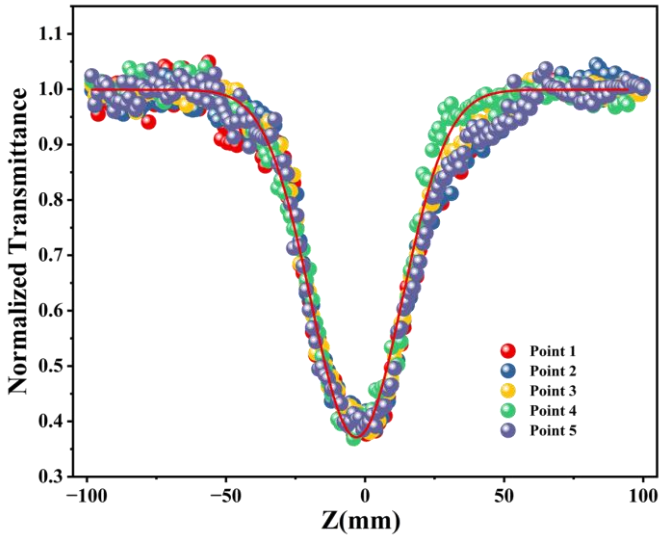

Figure S23 The open-aperture Z-scan results at 532 nm for **TOC-62** thin film: the same thin film is tested at different points.

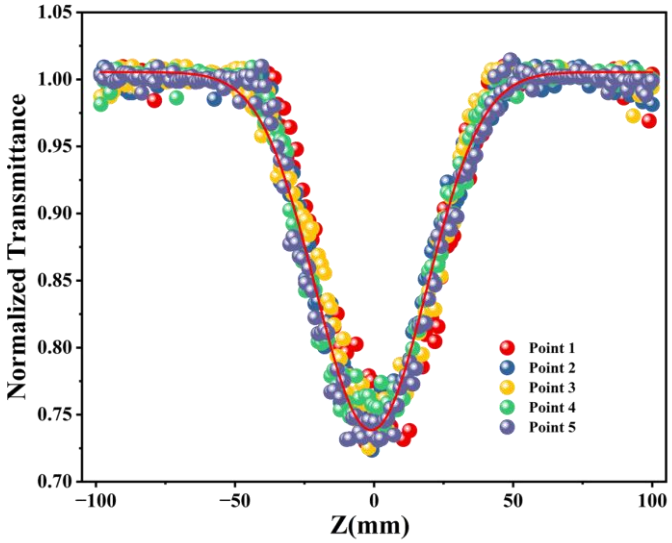

Figure S24 The open-aperture Z-scan results at 532 nm for **TOC-63** thin film: the same thin film is tested at different points.

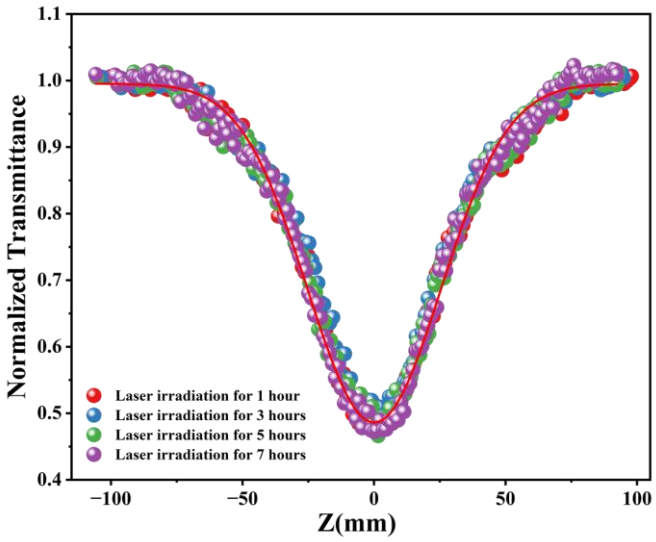

Figure S25 The open-aperture Z-scan results at 532 nm for **TOC-61** thin film: the same thin film is tested for different laser irradiation times at the same point.

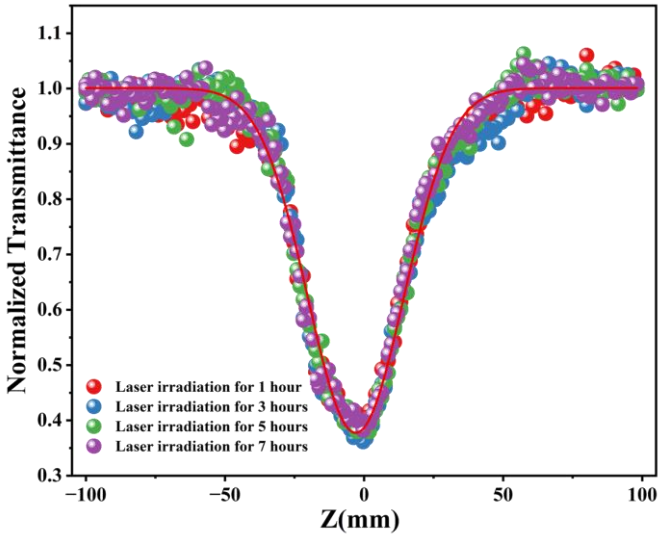

Figure S26 The open-aperture Z-scan results at 532 nm for **TOC-62** thin film: the same thin film is tested for different laser irradiation times at the same point.

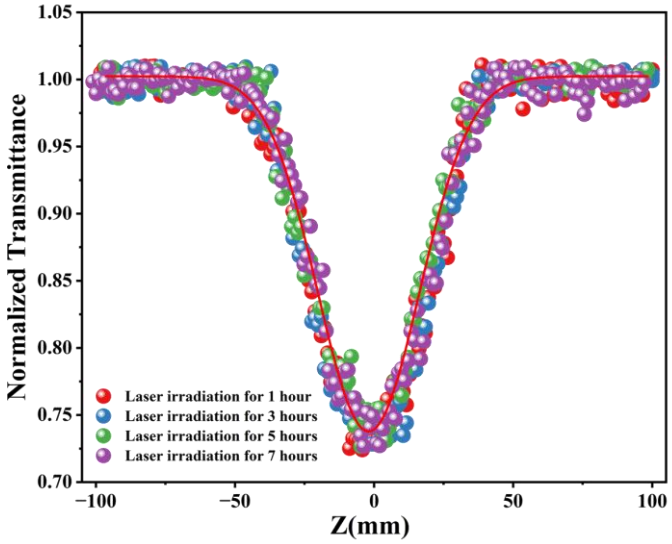

Figure S27 The open-aperture Z-scan results at 532 nm for **TOC-63** thin film: the same thin film is tested for different laser irradiation times at the same point.