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Heterometallic Al_6Zn_{12} nano-plate with π-conjugated ligand: synthesis and nonlinear absorption properties

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Table of content

Materials and Methods

All reagents were commercially and used without further purification. 3-hydroxy-2-naphthoic acid was purchased from Adamas-beta, while aluminium isopropoxide and zinc acetate dihydrate were acquired from Aladdin Chemical Reagent Shanghai. Benzyl alcohol (≥99%) was acquired from Sinopharm Chemical Reagent Beijing. The energy dispersive spectroscopy (EDS) analyses of single crystals were performed on a JEOL JSM6700F field-emission scanning electron microscope equipped with an Oxford INCA system. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ = 1.54056 Å) under ambient conditions. ICP analysis was conducted by using Inductively Coupled Plasma MS spectrometer (Agilent 7700). The UV-vis diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100 % reflectance) on a Perkin Elmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The absorption data are calculated from the Kubelka-Munk function, ($F(R) = (1-R)^2/2R$),[1] where R representing the reflectance. Elemental analysis (C and H) was carried out on a Vario Micro E III analyzer.

X-ray Crystallographic Analyses: Crystallographic data of crystal **AlOC-57** was collected on Hybrid Pixel Array detector equipped with Ga-Kα radiation (λ = 1.3405 Å) at about 100 K. The structures were solved with the dual-direct methods using ShelXT and refined with the full-matrix least-squares technique based on F^2 using the *SHELXL*-2014.[2] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically, riding on the concerned atoms, and refined with fixed thermal factors. All absorption corrections were performed using the multi-scan program.

Nonlinear Optical Measurements: The nonlinear optical property of samples was evaluated using the open-aperture Z-scan technique. The excitation light source was an Nd:YAG laser with a repetition rate of 10 Hz. The laser pulses (period, 8.5 ns; wavelength, 532 nm) were split into two beams with a mirror. The pulse energies at the front and back of the samples were monitored using energy detectors 1 and 2. All of the measurements were conducted at room temperature. The samples for nonlinear optical measurement were prepared by mixed **AlOC-57** with KBr, the mixture was ground and tableted to obtain a transparent round tablet as a test sample. Then the samples were mounted on a computer-controlled translation stage that shifted each sample along the z-axis.

$$T(Z, S=1) = \frac{1}{\sqrt{\pi}(Z,0)} \int_{-\infty}^{\infty} Ln\left[1 + q_0(Z,0)e^{-r^2}\right]dr \quad (1)$$

$$q_0(Z,0) = \beta I_0 L_{eff} \quad (2)$$

$$L_{eff} = \frac{1 - e^{-\alpha l}}{\alpha} \quad (3)$$

$$z_0 = \frac{k\omega_0^2}{2} \quad (4)$$

$$T(Z, \Delta\Phi) = 1 + \frac{4\Delta\Phi x}{(x^2 + 9)(x^2 + 1)} \quad (5)$$

$$\Delta\Phi = 2\pi\gamma I_0 L_{eff}/\lambda \quad (6)$$

$$\chi_R^{(3)} = \frac{4n_0^2\varepsilon_0 c}{3} n_2 \quad (7)$$

$$\chi_I^{(3)} = \frac{2n_0^2\varepsilon_0 c^2}{3\omega} \beta \quad (8)$$

$$\chi^{(3)}(esu) = \sqrt{(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2} \quad (9)$$

In these equations, I_0 is the on-axis peak intensity at the focus (Z = 0), L_{eff} is the effective thickness of the sample, l is the sample thickness, and α_0 is the linear absorption coefficient, x = z/z_0, z is the Z-scan displacement. z is the Z-scan displacement, $\Delta\Phi$ is the phase change, ε_0 is the permittivity of vacuum, c is the speed of light, $n_2(esu) = \frac{cn_0}{40\pi}\gamma(m^2/W)$, n_0 is the refractive index of the medium. By fitting the curves, the nonlinear absorption coefficient β, the nonlinear refractive coefficient γ and the third-order nonlinear susceptibilities $\chi^{(3)}$ were obtained.

References:

[1] W. W. Wendlandt and H. G. Hecht, *Anal. Chim. Acta*, 1967, **39**, 408-408.

[2] G. M. Sheldrick, *Acta Cryst*. C 2015, **71**, 3-8.

Supporting Figures:

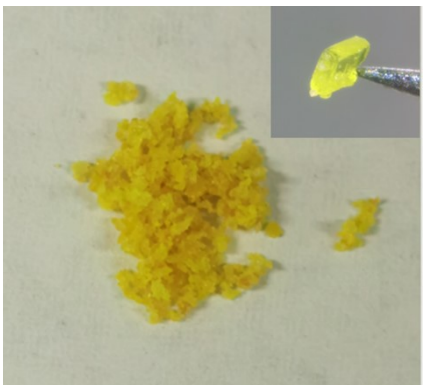

Fig. S1 Crystallographic photos of **AlOC-57.**

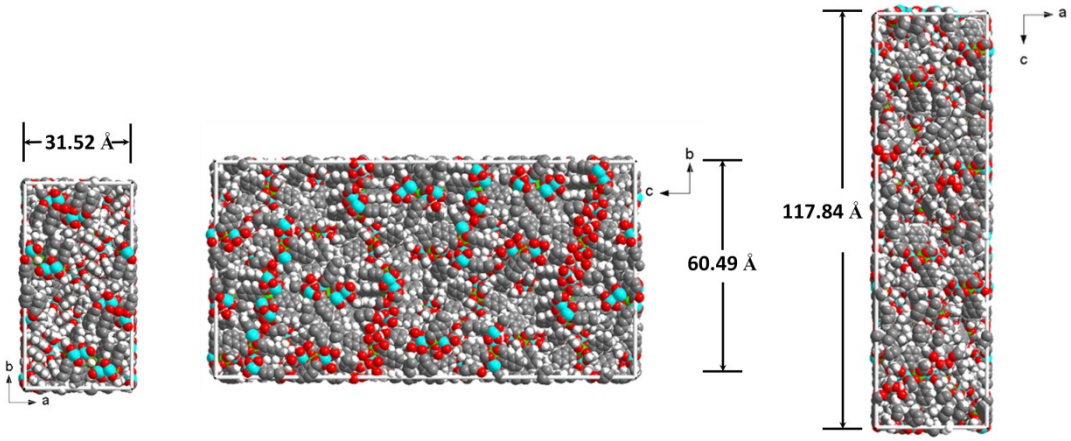

Fig. S2 The unit cell of **AlOC-57** showing in three axis directions (a-axis, b-axis and c-axis from left to right).

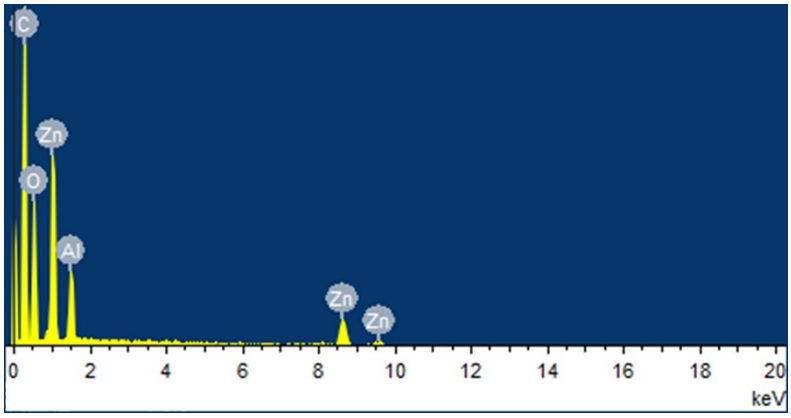

Fig. S3 EDS spectrum of **AlOC-57.**

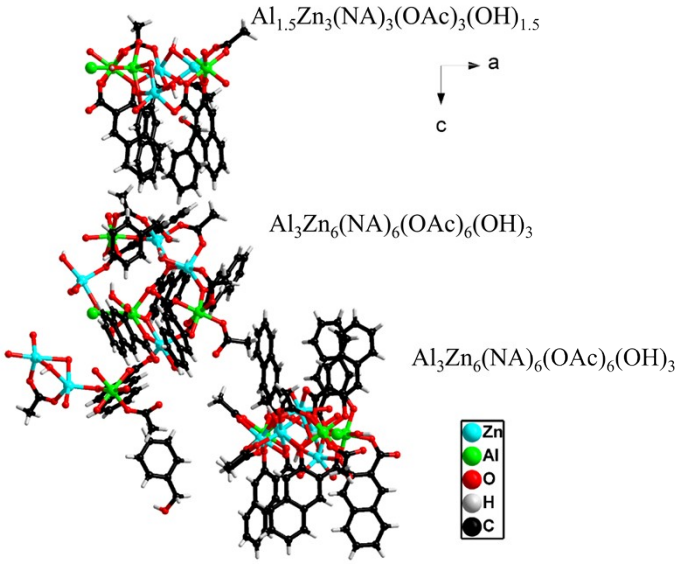

Fig. S4 The asymmetric unit of **AlOC-57**.

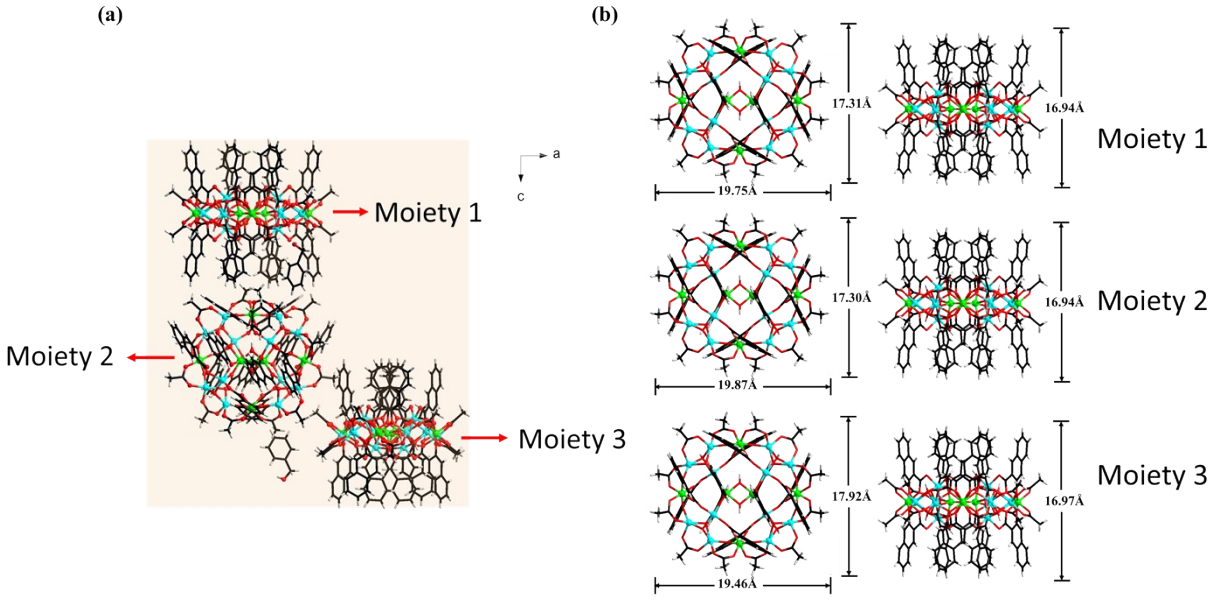

Fig. S5 The different orientations of the three moieties (a) and their respective sizes (b).

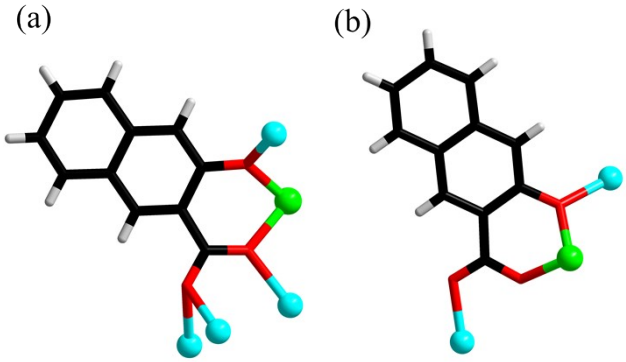

Fig. S6 Two coordination modes of L^{3-} ligands (μ_5-η^2:η^2:η^2 and μ_3-η^1:η^1:η^2).

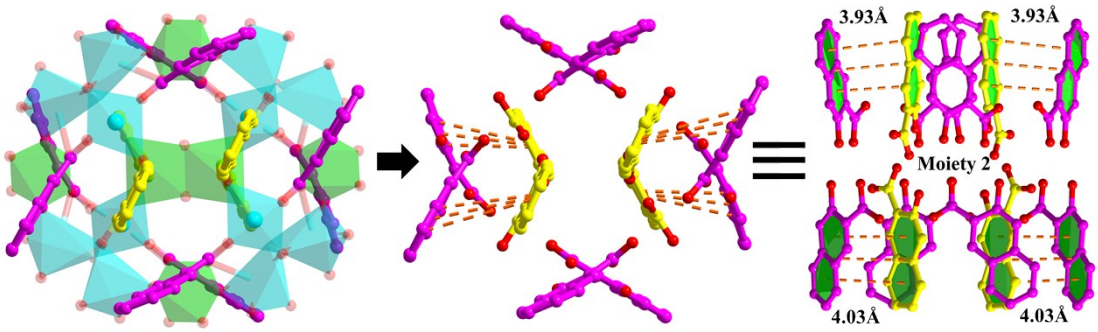

Fig. S7 Four pairs strong π···π interactions between the NA^{2-} ligands in each $\{Zn_{12}Al_6\}$ cluster (Due to the similar structure of the three moieties, moiety 2 is introduced here as a representative).

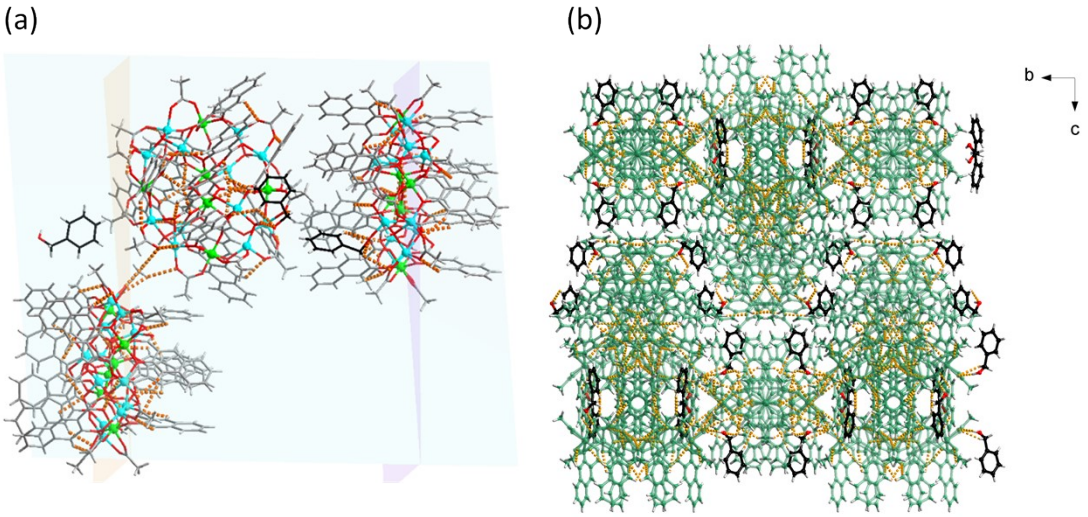

Fig. S8 The hydrogen bonding force in three moieties (a) and the packing mode (b).

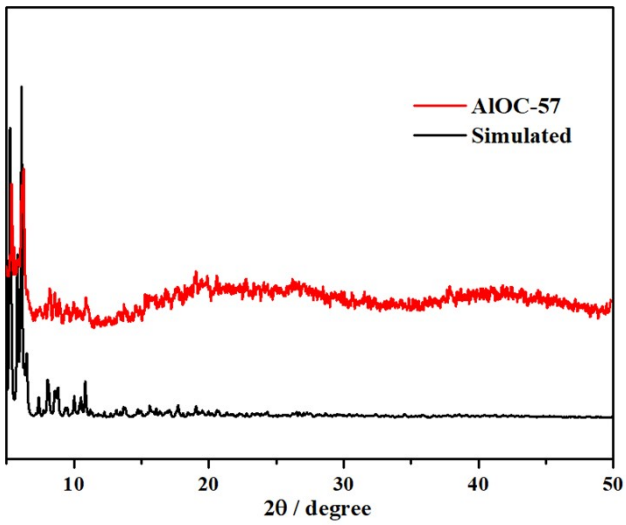

Fig. S9 PXRD spectra for **AlOC-57**.

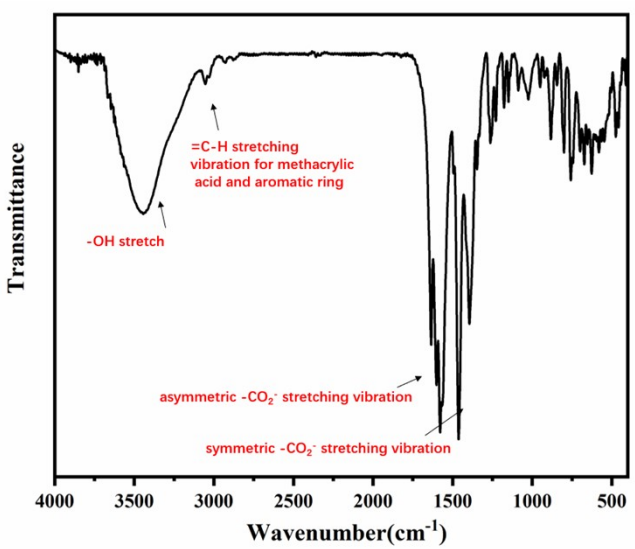

Fig. S10 FT-IR spectra of **AlOC-57**.

Discussion for IR spectra: The IR spectra of **AlOC-57** have been recorded in the range of 4000–400 cm^{-1} from solid samples palletized with KBr. The vibration at 3054 cm^{-1} is assigned to the =C-H vibration of the aromatic ring. the aboard absorption band from 3441 cm^{-1} stem from the ν(O-H) stretching of -OH groups on benzyl alcohol; the band at 1573 cm^{-1} and 1458 cm^{-1} can be ascribed to the asymmetric stretching vibration (ν_{as}) and symmetric stretching vibration (ν_s) of carboxylate group.

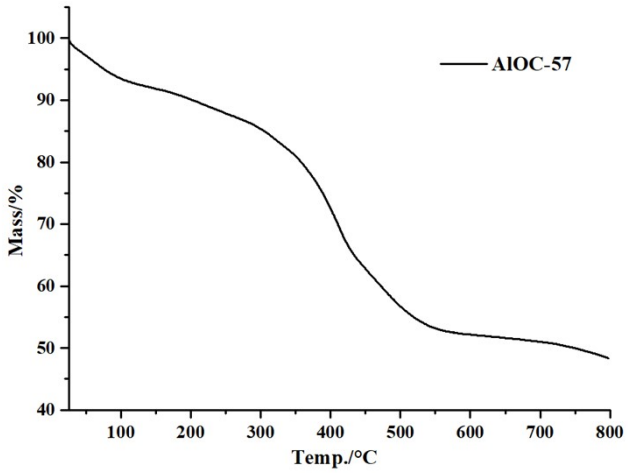

Fig. S11 The TGA spectra of **AlOC-57**.

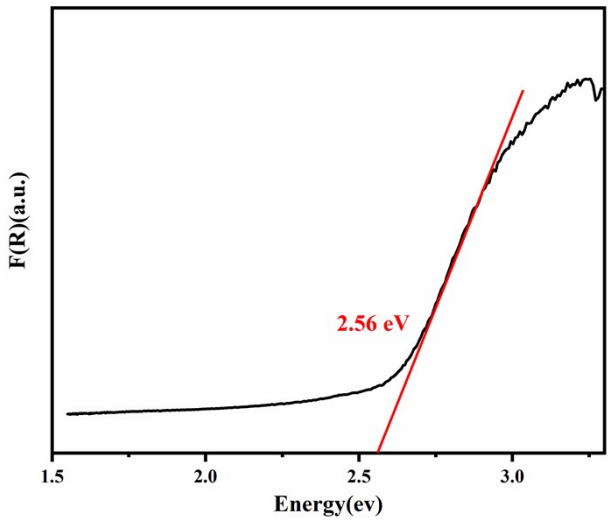

Fig. S12 The solid-state absorption spectra of **AlOC-57**.

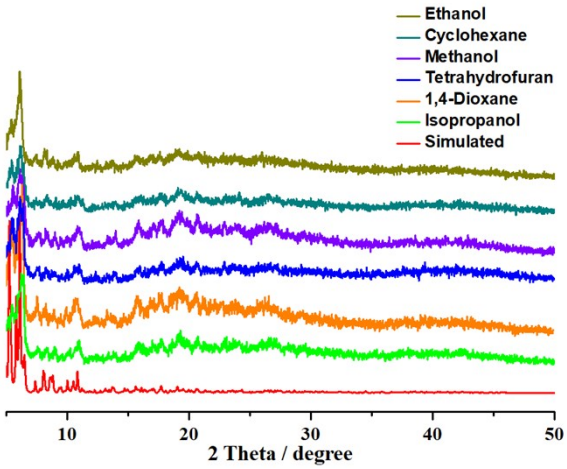

Fig. S13 The PXRD patterns of **AlOC-57** in different organic solvents at room temperature for three days.

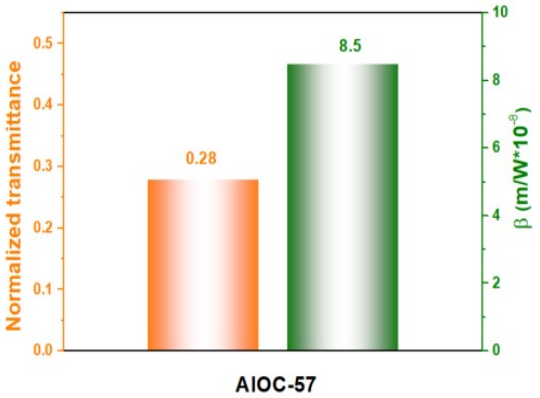

Fig. S14 Comparison of nonlinear transmittance and nonlinear absorption coefficients (β) of **AlOC-57**.

Supporting Tables:

Tab. S1 Selected bond lengths (Å) and BVS calculations in **AlOC-57.**

AlOC-57							
Zn13-O1	2.093	0.349	1.927	Zn1-O57^{iii}	2.481	0.122	1.924
Zn13-O2^{i}	2.134	0.312		Zn1-O62	2.002	0.446	
Zn13-O4^{ii}	2.01	0.437		Zn1-O67	1.998	0.451	
Zn13-O14	2.035	0.408		Zn1-O72	1.972	0.484	
Zn13-O24^{i}	2.026	0.418		Zn1-O81	2.026	0.418	
Zn10-O9	2.142	0.306	1.935	Al3-O1^{i}	1.841	0.550	2.888
Zn10-O10	2.088	0.354		Al3-O1	1.841	0.550	
Zn10-O19	1.993	0.457		Al3-O2^{i}	2.006	0.352	
Zn10-O29	2.035	0.409		Al3-O2	2.006	0.352	
Zn10-O34^{ii}	2.035	0.409		Al3-O3	1.847	0.541	
Zn8-O13	2.194	0.266	2.004	Al3-O3^{ii}	1.847	0.541	
Zn8-O23	2.019	0.426		Al1-O5	1.88	0.495	2.957
Zn8-O28	2.025	0.420		Al1-O5^{iv}	1.88	0.495	
Zn8-O33	2.032	0.412		Al1-O6^{iv}	1.868	0.511	
Zn8-O46	1.976	0.479		Al1-O6	1.868	0.5117	
Zn14-O16	2.332	0.183	1.929	Al1-O15	1.898	0.472	
Zn14-O24	2.017	0.429		Al1-O15^{iv}	1.898	0.472	
Zn14-O26	2.026	0.418		Al5-O8	1.851	0.535	2.897
Zn14-O37	2.014	0.432		Al5-O9	1.99	0.368	
Zn14-O43	1.987	0.465		Al5-O10	1.842	0.548	
Zn15-O5	2.008	0.439	2.004	Al5-O17	1.996	0.3619	
Zn15-O16	2.25	0.228		Al5-O18	1.849	0.538	
Zn15-O24	2.015	0.431		Al5-O20	1.845	0.54	
Zn15-O45	1.979	0.475		Al4-O23	1.875	0.502	2.98
Zn15-O48	2.017	0.429		Al4-O23^{ii}	1.875	0.502	
Zn11-O7^{ii}	2.187	0.271	2.004	Al4-O30	1.87	0.508	
Zn11-O12	2.034	0.409		Al4-O30^{ii}	1.87	0.508	
Zn11-O31	1.983	0.470		Al4-O36^{ii}	1.892	0.479	
Zn11-O34	2.045	0.397		Al4-O36	1.892	0.479	
Zn11-O38^{ii}	1.995	0.455		Al10-O12^{ii}	1.874	0.503	2.984
Zn9-O11	1.994	0.456	1.932	Al10-O12	1.874	0.503	
Zn9-O17^{ii}	2.12	0.324		Al10-O21	1.862	0.519	
Zn9-O20^{ii}	2.128	0.317		Al10-O21^{ii}	1.862	0.519	
Zn9-O22^{ii}	2.02	0.425		Al10-O40	1.9	0.469	
Zn9-O33^{ii}	2.036	0.407		Al10-O40^{ii}	1.9	0.469	
Zn4-O32	2.1	0.342	2.004	Al2-O25	1.9	0.4691	2.957
Zn4-O47	2.097	0.345		Al2-O25^{i}	1.9	0.469	
Zn4-O53	2.032	0.412		Al2-O26	1.868	0.511	
Zn4-O58^{iii}	2.017	0.429		Al2-O26^{i}	1.867	0.512	
Zn4-O59	1.98	0.474		Al2-O35	1.878	0.497	
Zn7-O13	2.41	0.148	1.944	Al2-O35^{i}	1.879	0.496	

Zn7-O33	1.985	0.467		Al6-O27	1.887	0.485	2.943
Zn7-O41	2.006	0.442		Al6-O39	1.902	0.466	
Zn7-O61	1.995	0.455		Al6-O41	1.875	0.501	
Zn7-O73	2.016	0.430		Al6-O42	1.904	0.464	
Zn12-O7^{ii}	2.344	0.177	1.974	Al6-O49	1.857	0.527	
Zn12-O27^{ii}	2.014	0.432		Al6-O54	1.878	0.497	
Zn12-O34	2.018	0.427		Al8-O32	1.841	0.550	2.897
Zn12-O65	1.976	0.479		Al8-O44	1.843	0.547	
Zn12-O78^{ii}	1.994	0.456		Al8-O47	2.021	0.338	
Zn2-O44^{iii}	2.086	0.356	1.946	Al8-O50	1.991	0.366	
Zn2-O50^{iii}	2.136	0.311		Al8-O51^{iii}	1.843	0.547	
Zn2-O63	2.035	0.408		Al8-O51	1.843	0.547	
Zn2-O67	2.021	0.424		Al7-O56	1.889	0.483	2.947
Zn2-O69	2.003	0.445		Al7-O62	1.887	0.485	
Zn5-O53	2.028	0.416	1.978	Al7-O70	1.898	0.4717	
Zn5-O55	2.194	0.265		Al7-O77	1.886	0.487	
Zn5-O60	2.031	0.413		Al7-O79	1.862	0.520	
Zn5-O74	2.007	0.441		Al7-O82	1.877	0.49916	
Zn5-O83	2.006	0.442		Al9-O52	1.932	0.430	2.879
Zn3-O57^{iii}	2.198	0.263	2.019	Al9-O60	1.881	0.493	
Zn3-O64	2.014	0.432		Al9-O64	1.891	0.480	
Zn3-O67	2.014	0.432		Al9-O66	1.873	0.504	
Zn3-O75	1.989	0.462		Al9-O68	1.874	0.503	
Zn3-O80	2.018	0.427		Al9-O71	1.902	0.466	
Zn6-O53	1.966	0.492	2.000	Calculated using r_o values of 1.704 Å for Zn^{2+}–O and 1.62 Å for Al^{3+}–O.			
Zn6-O55	2.444	0.135					
Zn6-O77^{iii}	1.999	0.450					
Zn6-O84	1.983	0.470					
Zn6-O85^{iii}	1.998	0.451					

Symmetry codes: (i) *x*, −*y*+5/4, −*z*+1/4; (ii) −*x*+1/4, −*y*+5/4, *z*; (iii) −*x*+5/4, −*y*+5/4, *z*; (iv) −*x*+1/4, *y*, −*z*+1/4.

Tab. S2. Hydrogen bond parameters for **AlOC-57**.

D–H···A	ARU-code	d(D–H)	d(D···A)	d(H···A)	<(DHA)
O(3)–H(3)···O(15)	2565	0.86	3.129(5)	2.38	146
O(3)–H(3)···O(15)	3565	0.86	3.129(5)	2.38	146
O(8)–H(8)···O(40)		0.86	3.103(4)	2.36	146
O(8)–H(8)···O(40)	2565	0.86	3.103(4)	2.36	146
O(18)–H(18)···O(36)		0.86	3.140(5)	2.39	146
O(18)–H(18)···O(36)	2565	0.86	3.140(5)	2.39	146
O(24)–H(24)···O(76)	3565	0.91	2.707(5)	1.80	179
O(33)–H(33)···O(86)	1555	0.91	2.687(8)	1.83	156
O(51)–H(51)···O(52)		0.86	3.210(5)	2.46	146
O(51)–H(51)···O(71)		0.86	3.174(6)	2.42	147
O(53)–H(53A)···O(87)	20555	0.91	2.720(5)	1.81	175
O(76)–H(76)···O(85)	13665	0.82	2.982(6)	2.21	158
C(103)–H(10A)···O(74)	8464	0.96	3.290(7)	2.57	132
C(177)–H(17F)···O(65)	2565	0.96	3.437(10)	2.51	161
C(198)–H(19G)···O(37)	15655	0.96	3.209(8)	2.40	142

C(198)–H(19H)···O(43)	15655	0.96	3.258(9)	2.59	127
C(201)–H(20M)···O(28)		0.97	3.329(12)	2.52	141
C(28)–H(28)···O(4)		0.93	2.749(6)	2.43	100
C(29)–H(29)···O(45)		0.93	3.254 (7)	2.44	146
C(32)–H(32)···O(11)		0.93	2.769(7)	2.45	100
C(34)–H(34A)···O(31)		0.93	3.283(7)	2.49	143
C(35)–H(35)···O(13)		0.93	2.735(7)	2.42	100
C(41)–H(41)···O(16)		0.93	2.741(6)	2.42	100
C(43)–H(43)···O(19)		0.93	2.774(6)	2.46	100
C(52)–H(52)···O(43)		0.93	3.154(6)	2.43	135
C(60)–H(60)···O(7)		0.93	2.720(6)	2.40	100
C(65)–H(165)···O(46)		0.93	3.234(6)	2.42	146
C(105)–H(105)···O(61)		0.93	3.189(7)	2.48	133
C(106)–H(106)···O(75)		0.93	3.269(7)	2.43	151
C(107)–H(207)···O(69)	2565	0.93	3.230(7)	2.53	132
C(112)–H(112)···O(59)		0.93	2.720(7)	2.39	101
C(133)–H(133)···O(57)		0.93	2.751(7)	2.44	100
C(134)–H(134)···O(55)		0.93	2.744(7)	2.42	100
C(143)–H(143)···O(65)	2565	0.93	3.210(7)	2.50	133
C(148)–H(148)···O(83)		0.93	3.157(8)	2.40	138
C(149)–H(149)···O(69)		0.93	2.729(7)	2.39	101
C(157)–H(157)···O(72)		0.93	3.189(8)	2.51	130
C(167)–H(167)···O(22)		0.93	3.353(7)	2.57	143
C(167)–H(167)···O(86)		0.93	2.649(10)	2.26	104
C(182)–H(182)···O(75)	20555	0.93	3.234(9)	2.56	130

ARU codes: (2565) 1/4-x, 5/4-y, z; (3565) x, 5/4-y, 1/4-z; (2665) 5/4-x, 5/4-y, z; (8464) -1/4+x, 1-y, -1/4+z; (20555) 3/4-x, y, 3/4-z; (15655) 1-x, 1/4+y, 1/4+z; (13655) 1-x, 3/2-y, 1/2-z.

Tab. S3 ICP analysis for **AlOC-57** (The error may be caused by trace impurities)

	AlOC-57	Cal.
Wt%	Zn: 17.33	Zn:18.46
	Al: 4.05	Al:3.80
Zn/Al	1.81:1	2:1

Tab. S4 The third-order NLO parameters of **AlOC-57**

Compound	Mass ratio (KBr:**AlOC-57**)	Sample thickness (mm)	Linear Transmittance I_0	Linear absorption coefficient α_0 (cm^{-1})	Laser energy E (μJ)	β (10^{-8} mW^{-1})	γ (10^{-14} esu)	$\chi^{(3)}$ (10^{-8} esu)	n_2(10^{-8} m^2W^{-1})
AlOC-57	20:1	0.06	0.2	33.33	80	8.5	1.5	3.1	5.55