

Supplementary Information

***Structure and optical limiting effects of heterometallic
Ag₆@Ti₁₂ and Ag₈@Ti₁₂ oxo clusters regulated by alkynyl
ligands***

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Experimental Section

Materials and Instrumentation.

All the reagents and solvents employed were purchased commercially and used as received without further purification. Silver acetate, 2-Picolinic acid, 1-Hexyne, 3-chlorophenylacetylene, benzoic acid, and $Ti(OiPr)_4$ were purchased from Adamas, while acetonitrile, 1-Propanol, and acetic acid were bought from Sino pharm Chemical Reagent Beijing. Powder X-ray diffraction (PXRD) analyses data were mounted on a Rigaku Mini Flex II diffractometer using $Cu-K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) collected with the angular range (2θ) from 3° to 50° at 298 K. Fourier transform infrared spectroscopy (FT-IR) data were collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer using KBr pellets ranging from 400 cm^{-1} to 4000 cm^{-1} . UV-vis diffuse reflectance data were recorded under ambient conditions using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lambda-950 UV spectrophotometer and scanned in the range 200–850 nm. The absorption data are calculated from the Kubelka-Munk function, $(F(R) = (1-R)^2/2R)$, [1] where R represents the reflectance. Elemental analysis (C, N and H) was carried out on a Vario Micro E III analyzer. ICP analysis was conducted by using Inductively Coupled Plasma MS spectrometer (Agilent 7700).

Z-scan measurements: The third-order nonlinear optical (NLO) absorption properties of the above sample were investigated by using the open-aperture (OA) Z-scan technique. The irradiation light source was an Nd: YAG laser with a repetition rate of 5 Hz. The laser pulse (period, 5 ns; wavelength, 532 nm) was split into two beams with a mirror. The pulse energies at the front and back of the samples were monitored by using two energy detectors. All of the measurements were conducted at room temperature. The $AgTiOCs@PDMS$ samples were mounted on a computer-controlled translation stage that shifted each sample along the z-axis.

Calculation of the nonlinear optical parameters. The relationship of the sample transmission and input fluence can be plotted from the open-aperture Z-scan curve. From the input laser pulse energy E_{in} and beam radius $\omega(z)$, the light fluence $F_{in}(z)$ at any position can be obtained.

$F_{in}(z)$ is defined as:

$$F_{in}(z) = \frac{4E_{in}\sqrt{\ln 2}}{\pi^2 \omega(z)^2}$$

Where $\omega(z)$ is defined as:

$$\omega(z) = \omega_0 \left[1 + \left(\frac{z}{z_0} \right)^2 \right]^{\frac{1}{2}}$$

Where ω_0 and z_0 are the light beam radius and the Rayleigh range, respectively, and z_0 is defined as:

$$z_0 = \frac{k\omega_0^2}{2}$$

Where k is defined as:

$$k = \frac{2\pi}{\lambda}$$

The equation fits for the nonlinear adsorption coefficient β as follows:

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

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

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

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, α is the linear absorption coefficient, and l is the sample thickness.

Synthesis of PTC-349: Silver acetate (0.06g, 0.36 mmol), 2-Picolinic acid (0.3 g, 2.4 mmol) and benzoic acid (0.05g, 0.41mmol) were dissolved in acetonitrile (7ml) and 1-Propanol (3ml), then 1-Hexyne (30 μ l), acetic acid (200 μ l) and Ti(OiPr)₄ (0.5 ml, 1.5 mmol) were added to the bottle and mixed at room temperature. The resultant solution was heated at 80°C for two days. After cooling to room temperature, colorless crystals of Ag₆Ti₁₂ were obtained (yield: ~49% based on Ti). Elemental analysis calcd (%) for C₁₁₄H₇₈Ag₆N₁₂O₅₄Ti₁₂ (MW 3699.768): C 36.97, N 4.54, H 3.64; found: C 32.66, N 3.91, H 3.68. (The proportion of hydrogen atoms has notably increased, while the proportions of carbon and nitrogen atoms have significantly decreased. We speculate that the crystal samples might contain some water. On one hand, it might absorb moisture during the placement process. On the other hand, while the crystal might contain water guests, their high degree of disorder makes it challenging to resolve them in single-crystal analysis, especially since the 'Squeeze' command has been utilized.)

Synthesis of PTC-350: Silver acetate (0.06g, 0.36 mmol) and 2-Picolinic acid (0.3 g, 2.4 mmol) were dissolved in acetonitrile (7ml) and 1-Propanol (3ml), 3-chlorophenylacetylene (40 μ l), acetic acid (200 μ l) and Ti(OiPr)₄ (0.5 ml, 1.5 mmol) were added to the bottle and mixed at room temperature. The resultant solution was heated at 80°C for five days. After cooling to room temperature, colorless crystals of PTC-350 were obtained (yield: ~52% based on Ti). Elemental analysis calcd (%) for C₁₀₀H₇₈Ag₈Cl₂N₁₂O₅₆Ti₁₂ (MW 3850.504): C 31.16, N 4.3, H 2.03 found: C 32.00, N 4.08, H 2.6.

X-ray Crystallographic Analyses: The structure determination of PTC-349 and PTC-350 was performed on a Hybrid Pixel Array detector equipped with Ga K α radiation ($\lambda = 1.3405 \text{ \AA}$) at about 100 K. Their structures were solved with direct methods using SHELXS-2014 and refined with the full-matrix least-squares technique based on F^2 using SHELXL-2014.^[1] 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. The diffused electron densities resulting from these residual cations and solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.^[2]

References:

- [1] G. M. Sheldrick, Acta Cryst. C 2015, **71**, 3-8.
- [2] Spek, A. L. PLATON, a multipurpose crystallographic tool; Utrecht University: 2001.

Supporting Figures:

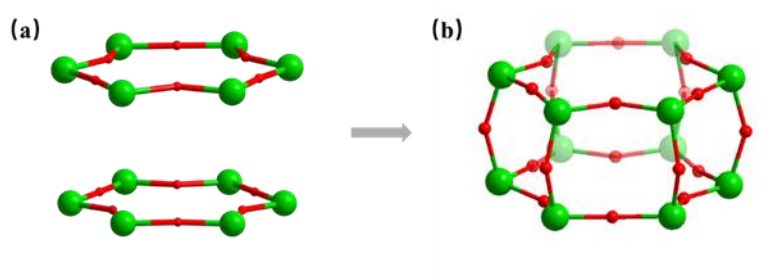


Fig. S1 Structural diagram of Ti_{12} -oxo core.

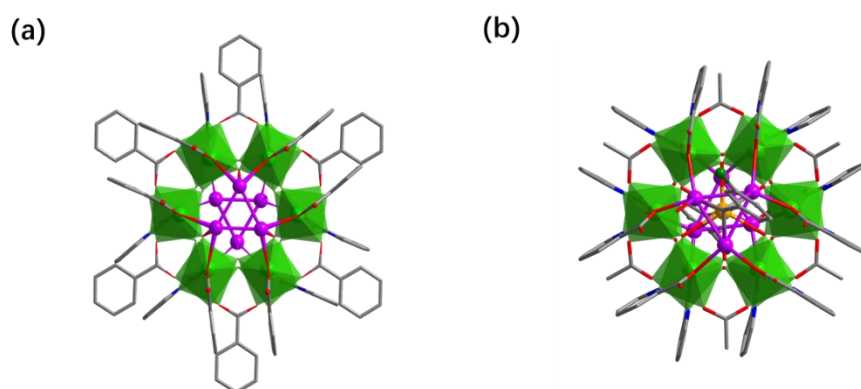


Fig. S2 Top views of the molecular structure of (a) PTC-349, (b) PTC-350.

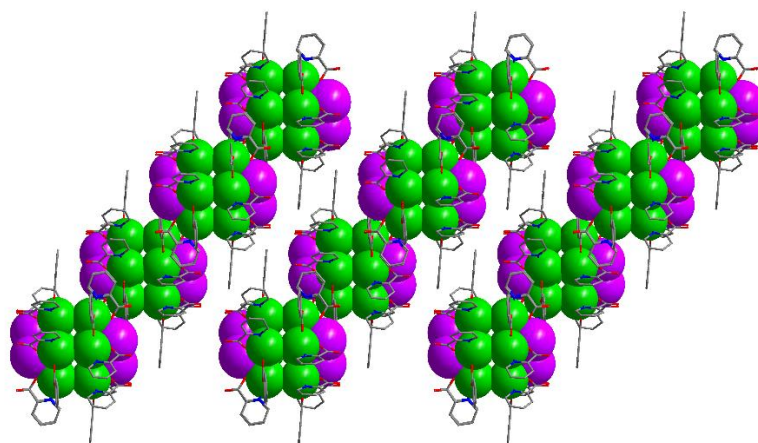


Fig. S3 The packing view of PTC-349 along a-axis.

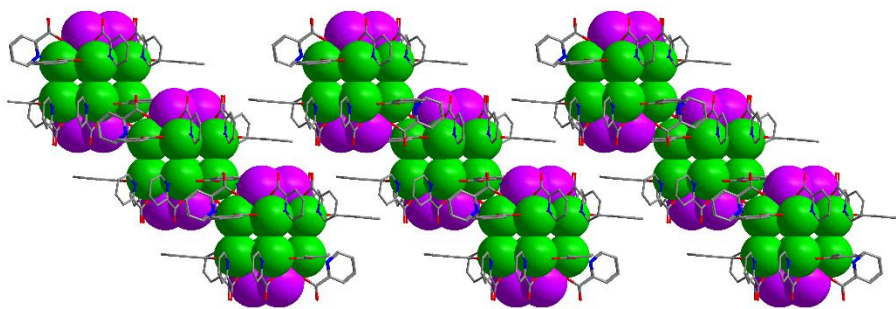


Fig. S4 The packing view of **PTC-349** along b-axis.

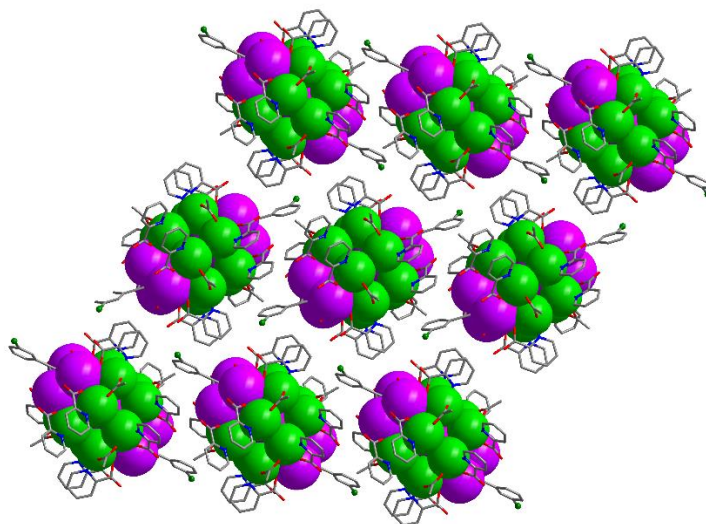
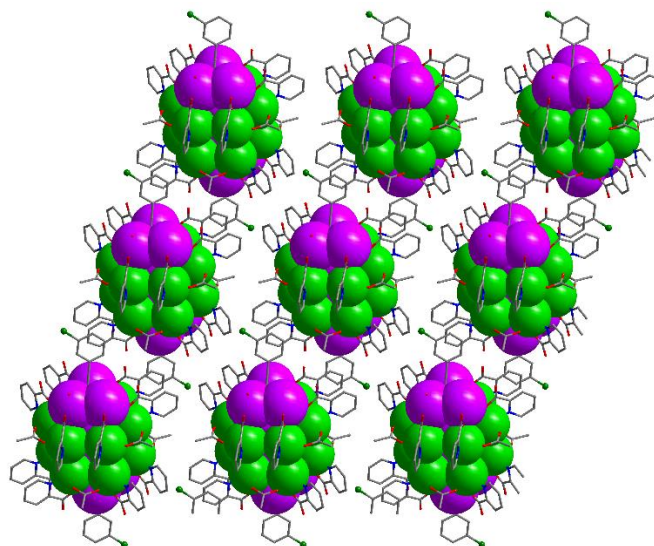


Fig. S5 The packing view of **PTC-350** along a-axis.



cc

Fig. S6 The packing view of **PTC-350** along b-axis.

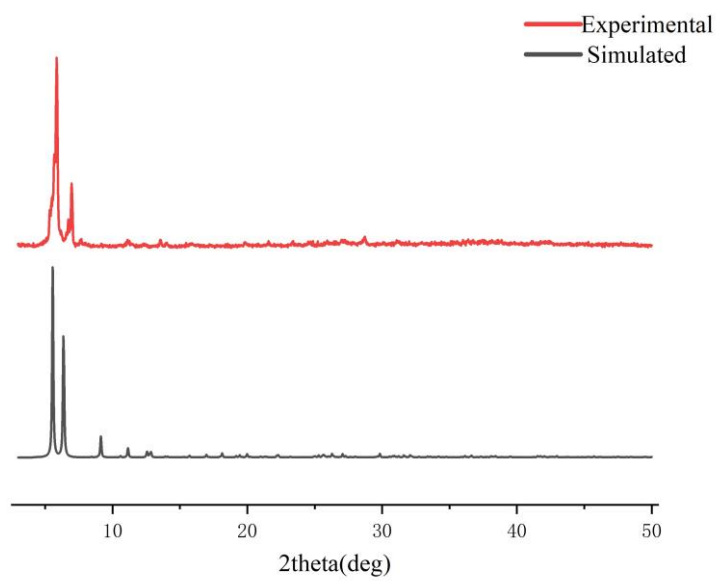


Fig. S7 The PXRD patterns of **PTC-349**.

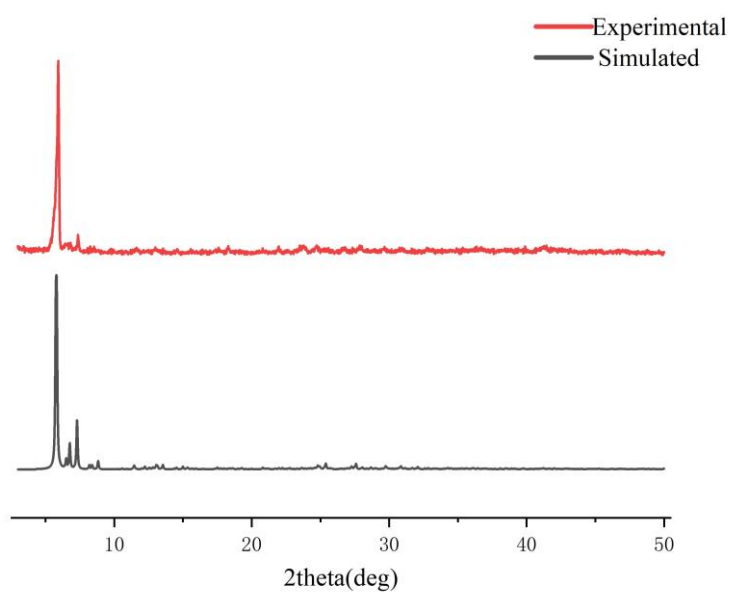


Fig. S8 The PXRD patterns of **PTC-350**.

In the high wavenumber region ($\nu > 1000 \text{ cm}^{-1}$), the weak absorption bands at $3745\text{--}3147 \text{ cm}^{-1}$ can be ascribed to the stretching vibrational modes of O-H bonds in hydroxyl groups. The characteristic stretching vibrations $\nu(\text{CO}_2^{2-})$ of in carboxylic groups and $\nu(\text{C}=\text{C})$ in benzene rings are overlapped from 1650 cm^{-1} to 1405 cm^{-1} . Among them, the asymmetric stretching vibration (ν^{as}) and symmetric stretching vibration (ν^{s}) of the carboxylate group can be attributed, namely, the band at $1569\text{--}1558 \text{ cm}^{-1}$ is assigned to the $\nu^{\text{as}}(\text{CO}_2^{2-})$ whilst the signal at $1438\text{--}1429 \text{ cm}^{-1}$ is ascribed to the $\nu^{\text{s}}(\text{CO}_2^{2-})$. The absorption peaks appearing at $638\text{--}1100 \text{ cm}^{-1}$ are assigned to the stretching vibrations of $\nu(\text{Ti-O})$.

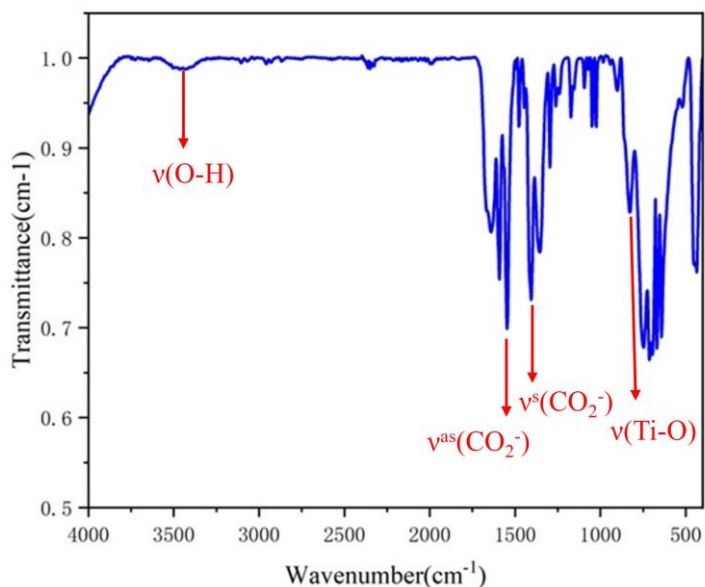


Fig. S9 The IR spectrum of PTC-349.

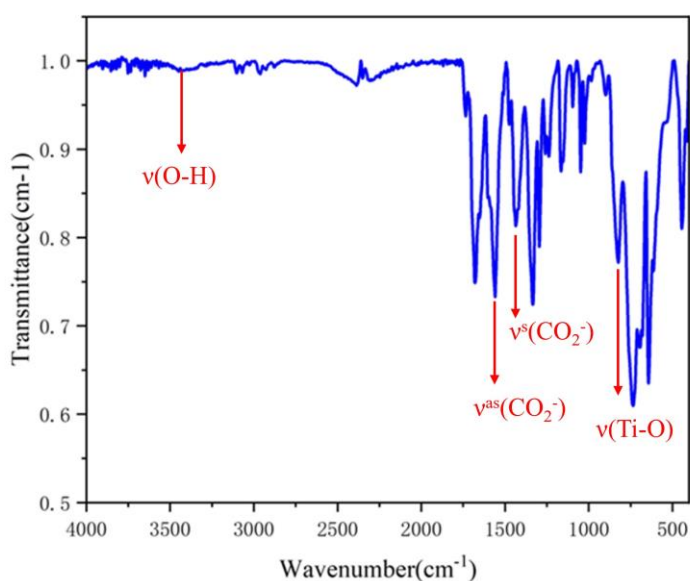


Fig. S10 The IR spectrum of PTC-350.

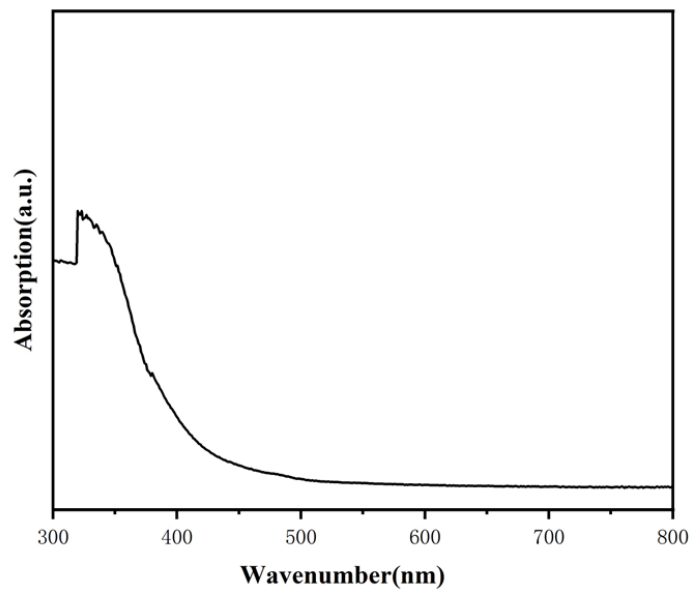


Fig. S11 The UV spectrum of **PTC-349**.

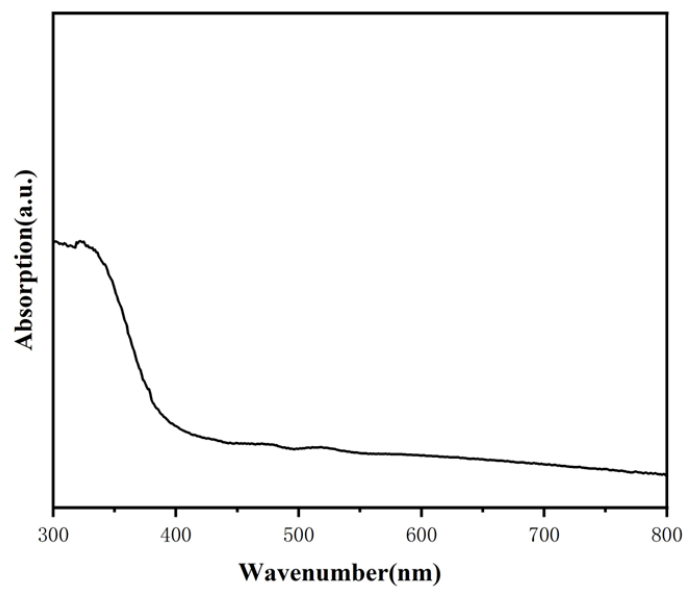


Fig. S12 The UV spectrum of **PTC-350**.

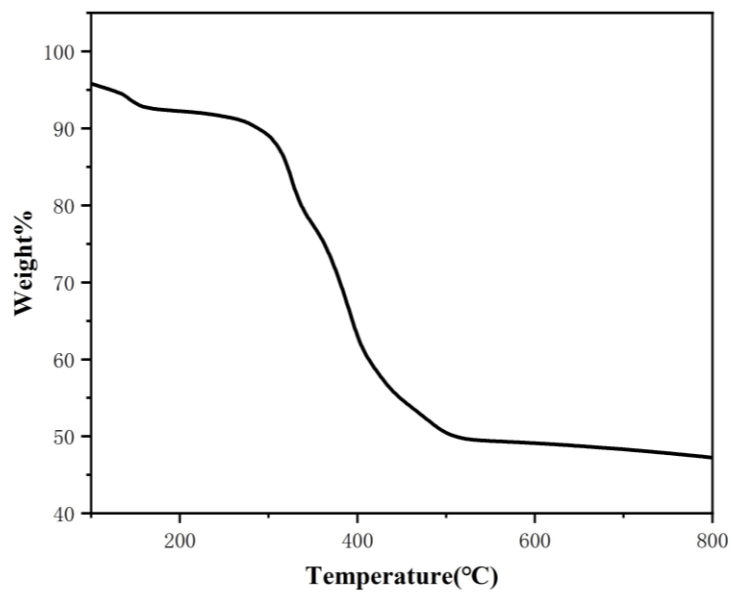


Fig. S13 The TGA curve of **PTC-349**.

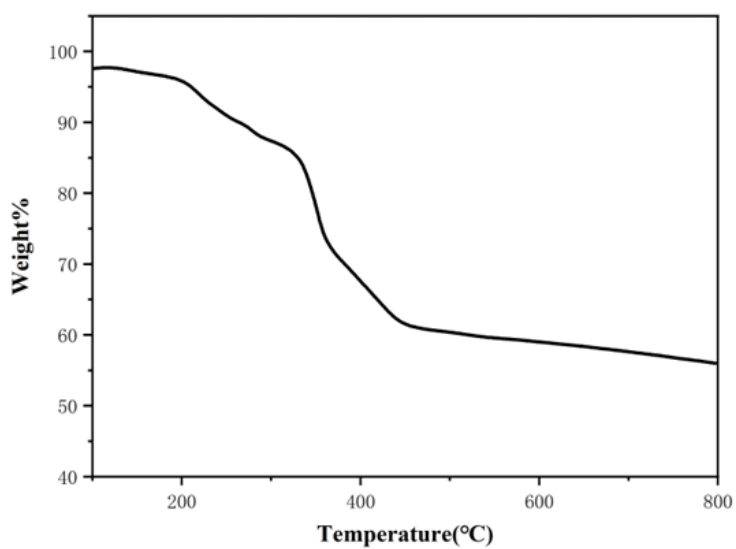


Fig. S14 The TGA curve of **PTC-350**.

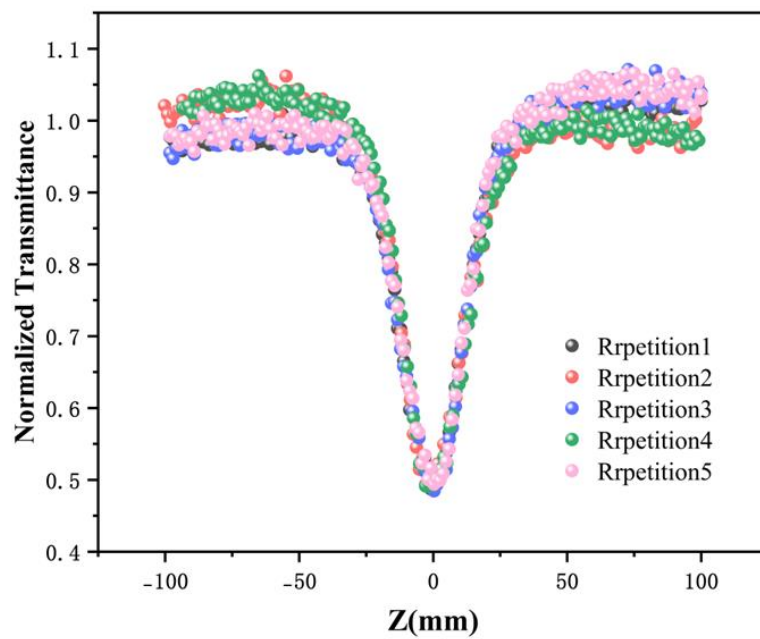


Fig. S15 The repeatability of fifth-order NLO responses for **PTC-349**.

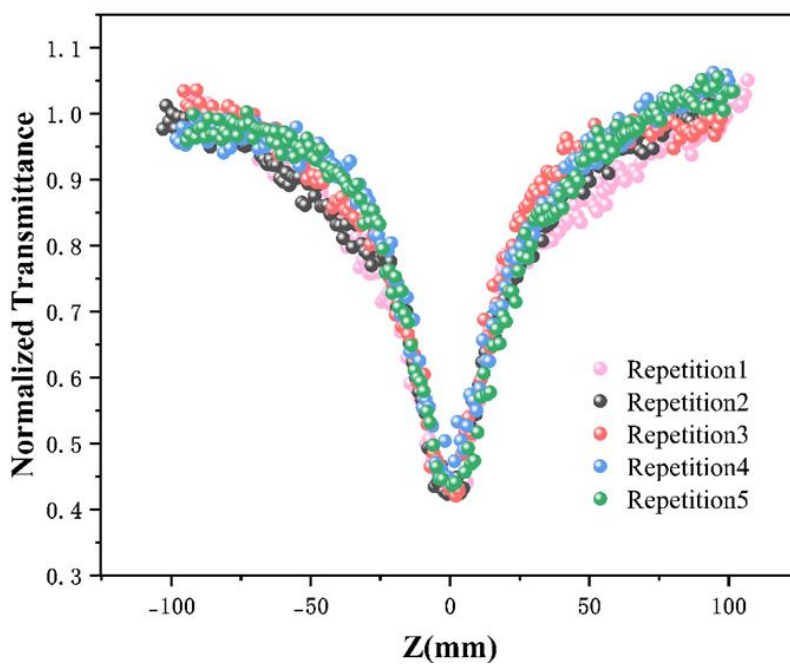


Fig. S16 The repeatability of fifth-order NLO responses for **PTC-350**.

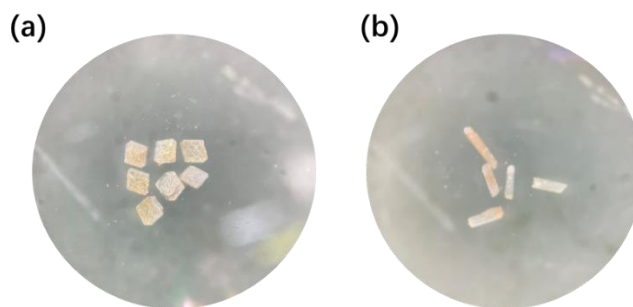


Fig. S17 Crystal diagrams of **PTC-349(a)** and **PTC-350(b)** screened using crystal sieves.

Supporting Table:

Tab. S1 Crystal data and structure refinement for **PTC-349** and **PTC-350**.

Compound	PTC-349	PTC-350
Crystal Formula	$C_{114}H_{78}Ag_6N_{12}O_{54}Ti_{12}$	$C_{100}H_{78}Ag_8Cl_2N_{12}O_{56}Ti_{12}$
Formula weight	3871.97	3852.40
Space group	R $\bar{3}c$	P $2_1/c$
Crystal system	Trigonal	Monoclinic
a/Å	27.7454 (3)	16.3284(2)
b/Å	27.7454 (3)	30.6769(3)
c/Å	42.2217 (7)	15.5639(2)
$\alpha /^\circ$	90	90
$\beta /^\circ$	90	111.7980(10)
$\gamma /^\circ$	120	90
V/Å ³	28148.0 (8)	7238.60(15)
Z	6	2
ρ /g cm ⁻³	1.371	1.767
μ /mm ⁻¹	1.160	10.092
F(000)	11436.0	3768.0
GOF on F ₂	1.034	1.027
R1[$I > 2\sigma(I)$] ^[a]	0.055	0.087
wR2[$I > 2\sigma(I)$] ^[b]	0.1831	0.2533
<p>[a] $R1 = \sum F_o - F_c / \sum F_o$. [b] $wR2 = \{\sum [w(F_o2 - F_c2)^2] / \sum [w(F_o2)^2]\}^{1/2}$</p>		

Tab. S2 Selected bond lengths (Å) in PTC-349.

Bond	Length/Å	Bond	Length/Å
Ag1A-Ag1A ⁱ	3.079(3)	Ag1A-O3	2.353(4)
Ag1A-Ag1A ⁱⁱ	3.079(3)	Ag1B ^{iv} -O8	2.573(4)
Ag1B-Ag1B ⁱ	2.716(6)	Ag1B ^{iv} -O5	2.386(4)
Ag1B-Ag1B ⁱⁱ	2.716(6)	Ag1B-O3	2.376(4)
Ag1A-O5 ⁱⁱⁱ	2.357(3)		

1(i) $-y+1, x-y, z$; (ii) $-x+y+1, -x+1, z$; (iii) $y+1/3, -x+y+2/3, -z+2/3$; (iv) $x-y+1/3, x-1/3, -z+2/3$.

Tab. S3 Selected bond lengths (Å) in PTC-350.

Bond	Length/Å	Bond	Length/Å
Ag1A-Ag2A	3.0562(17)	Ag2A-C1	2.130(13)
Ag1A-Ag3	2.9433(14)	Ag2A-000J ⁱ	2.313(5)
Ag1A-Ag4A	3.182(2)	Ag2A-0000 ⁱ	2.358(6)
Ag1B-Ag4B	2.900(5)	Ag2B-C1	2.655(14)
Ag2A-Ag3	3.1711(14)	Ag2B ^o -000J	2.168(9)
Ag2A-Ag4A	3.2899(16)	Ag2B ⁱ -0000	2.252(9)
Ag3-Ag4A	3.3162(16)	Ag3-C1	2.129(13)
Ag3-Ag4B	2.589(3)	Ag3-000Z	2.305(8)
Ag1A-C1	2.005(15)	Ag3-000V	2.317(6)
Ag1A-O1	2.400(8)	Ag4A-000F	2.537(5)
Ag1A-000R ⁱ	2.444(6)	Ag4A-000L ⁱ	2.506(6)
Ag1A-000T	2.315(6)	Ag4A-000M	2.501(6)
Ag1B-C1	2.377(13)	Ag4B-C1	2.604(17)
Ag1B ⁱ -000R	2.426(7)	Ag4B-000F	2.341(6)
Ag1B-000T	2.328(6)	C1-C2	1.26(2)

(i) $-x+1, -y+1, -z+1$.

Tab. S4 Optical limiting test data of **PTC-349** and **PTC-350**.

Sample	Ag₆Ti₁₂	Ag₈Ti₁₂
Linear transmittance	0.9	0.88
Thickness (mm)	2	2
OL threshold (J/cm ²)	2.57	0.67
Nonlinear transmittance	0.5	0.43
β (10 ⁻⁹ m/W)	0.6	0.95

Tab. S5 ICP data of **PTC-349** and **PTC-350**.

	Ag	Ti	Calcu(Ag:Ti)	Ag:Ti
PTC-347	13.63 w%	11.39 w%	1.13	1.19
PTC-350	18.90 w%	12.18 w%	1.5	1.55