Supporting Information

Modification of Metallic and Non-metallic Sites in Pentasupertetrahedral Chalcogenidometalate Clusters for Third-Order Nonlinear Optical Response

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Section S1: General Methods

Chemicals and Instrumentation

All chemicals used were analytical reagent and were used without further purification. Butyltin trichloride (n-$BuSnCl_3$, 97%), $Ga(NO_3)_3 \cdot xH_2O$ (99.9%), SeO_2 (99%), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 98%), 3-dimethylaminopropylamine (DMAPA, 98%), 1,1,4,7,7-pentamethyl-diethylenetriamin (PMDETA, 98%) were acquired from Aladdin Chemical Reagent Shanghai, while CuCl (≥ 99.5%), CuI (≥ 99.5%), $InCl_3 \cdot 4H_2O$ (≥ 99.5%), $In(NO_3)_3 \cdot 4.5H_2O$ (≥ 99.5%), sulfur powder (≥ 99.5%), N,N-dimethylformamide (DMF, ≥ 99.5%), $InCl_3 \cdot 4H_2O$ (≥ 99.5%), ethylene glycol (EG, ≥ 99.5%), dimethyl sulfoxide (DMSO, ≥ 99.5%) were bought from Sinopharm Chemical Reagent Beijing. Powder X-ray diffraction (PXRD) data were collected on a Mini Flex-II diffractometer with Cu Kα radiation (λ = 1.54056 Å). The inductively coupled plasma (ICP) measurement was carried out on an Ultima-2 spectrometer. The elemental analyses (EA) of C/H/N/S were performed at a Vario Micro-E-III analyzer. The UV-vis diffuse reflectance spectra (UV-Vis DRS) were measured on a Lambda 950 spectrophotometer, by using $BaSO_4$ as reflectance reference. The Fourier transformed-infrared spectra (FT-IR) were recorded with a Nicolet Magna 750 infrared spectrometer. The thermo-stability studies were implemented on a NETSCHZ STA-449C thermo-analyzer with a heating rate of 10 °C/min under a N_2 atmosphere from 25 °C to 800 °C. Electrospray ionization-mass (ESI-MS) were carried out on an Impact II UHR-TOF (Bruker) instrument. The morphology was characterized by a scanning electron microscopy (SEM, Phenom G2 Pro) and a transmission electron microscopy (TEM, JEM-2010F). The energy-dispersive spectra (EDS) analysis were performed on a JEOL JSM-6700F scanning electron microscope. The diameter distribution of the clusters in ethanol solution was determined via dynamic light scattering (DLS) measurement (Nano ZS ZEN3600, Malvern).

Photoelectric Response: Fluorine-doped tin oxide (FTO) glasses were cleaned by sonication in the acetone for 30 min and then dried at 60 °C over night. Then the FTO glasses were used as the working electrodes. 5 mg sample was dispersed in the 0.5 ml

ethanol and sonicated for 1 hour to get slurry. The conductive tape was used to adhere to part of FTO glasses to leave a circle with an area of 0.25 cm^2 for the slurry and then dried at room temperature naturally. The photocurrent measurements were performed in three electrodes electrochemical mode in the presence of 0.2 M Na_2SO_4 solution with a 532 nm laser. The electrochemical impedance spectroscopy (EIS) measurements were carried out an open-circuit voltage in the frequency range from 0.1 Hz to 100 kHz with an amplitude of 5 mV and the working electrode was illuminated with a 532 nm laser.

Z-scan Measurements: The third-order nonlinear optical (NLO) properties of the clusters were investigated by open-aperture (OA) Z-scan experiment. The excitation light source was an Nd:YAG laser with a repetition rate of 10 Hz. The laser beam (with a period of 8.5 ns and 532 nm wavelength) was split into two beams with a mirror. The energy detectors D1 and D2 receive signals from the front and back of the samples individually. The sample was fixed on a program-controlled rail that moved each sample along the z-axis. The Z-scan curves of each sample was measured as an 60% linear transmitting dispersion in ethanol in a 0.1 cm quartz cell at room temperature.

Section S2: Synthetic Procedures

All the title compounds were synthesized by similar procedures. n-$BuSnCl_3$ was used in air without any precautions. The mixture of reactants was sealed after stirring for 30 min (for **2-4** in a 20 mL vial, for **1** in a 23 mL Teflon-lined steel autoclave) and heated for several days then cooled to room temperature naturally.

(1) Synthesis of Compound **1** $[Sn_{11}In_9Cu_6S_{44}]$•11(H^+DBU)

Dark red rhombic crystals (yield: 25 mg, ca. 11% base on $In(NO_3)_3·4.5H_2O$) of **1** were obtained by the reaction of *n*-$BuSnCl_3$ (0.1 mL, 0.60 mmol, 0.1693g), CuI (0.3 mmol, 58 mg), $In(NO_3)_3·4.5H_2O$ (132 mg，0.35 mmol), sulfur powder (4 mmol, 128 mg), DMF (2 mL) and DBU (1 mL) at 160 °C for 12 days. EA data: C 18.99 %, H 3.02 %, N 5.03 %, S 24.15 %. ICP data: Sn 21.6 %, In 17.27 %, Cu 6.55 %.

(2) Synthesis of Compound **2** $[Sn_{10}In_{10}Cu_6Se_{44}]$•6($H_2^{2+}$DMAPA)•2(DMAPA)•9EG

Black cubic crystals (yield: 30 mg, ca. 39.58% base on $InCl_3·4H_2O$) of **2** were obtained by the reaction of *n*-$BuSnCl_3$ (0.1 mL, 0.60 mmol, 0.1693g), $InCl_3·4H_2O$ (29.3 mg，0.1 mmol), CuCl (10 mg, 0.1 mmol), SeO_2 (222 mg，2 mmol), EG (1 mL) and DMAPA (1.5 mL) at 100 °C for 7 days. EA data: C 9.25%, H 2.165%, N 2.94%. ICP data: Sn 15.78%, In 14.26%, Cu 5.31%, Se 45.83%.

(3) Synthesis of Compound **3** $[Sn_{10}In_{10}Cu_6S_{40}O_4]$•6[$H_2^{2+}$PMDETA]•10EG

Black cubic crystals (yield: 8 mg, ca. 16.74% base on CuCl) of **3** were obtained by the reaction of *n*-$BuSnCl_3$ (0.1 mL, 0.60 mmol, 0.1693g), $InCl_3·4H_2O$ (58.6 mg，0.2 mmol), CuCl (5 mg, 0.05 mmol), sulfur powder (96 mg, 3 mmol), EG (2 mL) and PMDETA (2 mL) at 100 °C for 7 days. EA data: C 15.77%, H 3.51%, N 4.44%, S 23.15 %. ICP data: Sn 16.33%, In 16.56%, Cu 6.56%.

(4) Synthesis of Compound **4** $[Sn_{10}Ga_{10}Cu_6S_{40}O_4]$•6($H_2^{2+}$DMAPA)•7EG

Black cubic crystals (yield: 10 mg, ca. 10.7% base on $Ga(NO_3)_3·xH_2O$) of **4** were obtained by the reaction of *n*-$BuSnCl_3$ (0.1 mL, 0.60 mmol, 0.1693 g), $Ga(NO_3)_3·xH_2O$ (50.5 mg，0.2 mmol), CuCl (19.8 mg, 0.2 mmol), sulfur powder (96 mg, 3 mmol), EG (2 mL) and DMAPA (1 mL) at 120 °C for 7 days. EA data: C 11.205%, H 2.675%, N 3.25%, S 24.34 %. ICP data: Sn 19.29%, Ga 12.91%, Cu

6.43%.

Section S3: Single Crystal X-Ray Diffraction (SCXRD)

Single crystals of the titled compounds were carefully selected under an optical microscope and glued to a thin glass fiber. SCXRD data were collected on a MM007-Saturn724+ diffractometer (for **3** and **4**) with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at room temperature, an Oxford diffractometer (for **1**) equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at room temperature. All the structures were solved by direct methods and refined on F^2 by full matrix least-squares using Olex2 program.[1-3] All the non-hydrogen atoms are refined anisotropically. All absorption corrections were performed using the multi-scan program. Contributions to scattering due to disordered solvent molecules were removed using the SQUEEZE routine of PLATON.[4] Structures were then refined again using the data generated.

Table S1. Crystallographic data of the P2 clusters

Compounds	**1**	**3**	**4**
CCDC#	2049115	2049116	2049117
Empirical formula	$C_{27}H_{51}Cu_6In_9N_6S_{44}Sn_{11}$	$Cu_6In_{10}O_4S_{40}Sn_{10}$	$Cu_6Ga_{10}O_4S_{40}Sn_{10}$
Formula weight	4590.58	4062.74	3611.04
Temperature/K	293(2)	293(2)	293(2)
Crystal system	triclinic	cubic	cubic
Space group	P-1	P-43m	P-43m
a/Å	16.3640(6)	16.7403(3)	15.3751(8)
b/Å	24.1311(7)	16.7403(3)	15.3751(8)
c/Å	24.2168(7)	16.7403(3)	15.3751(8)
α/°	86.704(2)	90	90
β/°	81.304(3)	90	90
γ/°	76.646(3)	90	90
Volume/Å^3	9194.7(5)	4691.3(3)	3634.6(6)
Z	2	1	1
ρ_{calc}g/cm^3	1.658	1.438	1.65
μ/mm^{-1}	3.759	3.621	4.939
F(000)	4248	1836	1656
Crystal size/mm^3	0.4 × 0.2 × 0.2	0.15 × 0.15 × 0.15	0.2 × 0.1 × 0.05
Radiation	Mo Kα	MoKα	MoKα
Radiation	(λ = 0.71073)	(λ = 0.71073)	(λ = 0.71073)
2Θ range for data collection/°	6.778 to 50.7	4.866 to 52.688	7.496 to 50.61
Index ranges	-19 ≤ h ≤ 19,	-20 ≤ h ≤ 17,	-14 ≤ h ≤ 18,
Index ranges	-29 ≤ k ≤ 27,	-20 ≤ k ≤ 20,	-18 ≤ k ≤ 18,
Reflections collected	-29 ≤ l ≤ 29	-20 ≤ l ≤ 20	-18 ≤ l ≤ 18
	67376	33287	20517
Independent reflections	33599 [R_{int} = 0.0365,	1846 [R_{int} = 0.0337,	1308 [R_{int} = 0.0402,
Independent reflections	R_{sigma} = 0.0717]	R_{sigma} = 0.0109]	R_{sigma} = 0.0128]
Data/restraints/parameters	33599/511/958	1846/9/42	1308/1/40
Goodness-of-fit on F^2	1.008	1.067	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0472,	R_1 = 0.0185,	R_1 = 0.0547,
Final R indexes [I>=2σ (I)]	wR_2 = 0.1175	wR_2 = 0.0496	wR_2 = 0.1538
Final R indexes [all data]	R_1 = 0.0854,	R_1 = 0.0187,	R_1 = 0.0550,
Final R indexes [all data]	wR_2 = 0.1327	wR_2 = 0.0496	wR_2 = 0.1540
Largest diff. peak/hole / e Å^{-3}	1.17/-1.06	0.31/-0.24	0.61/-1.40

Section S4: Powder X-Ray Diffraction (PXRD)

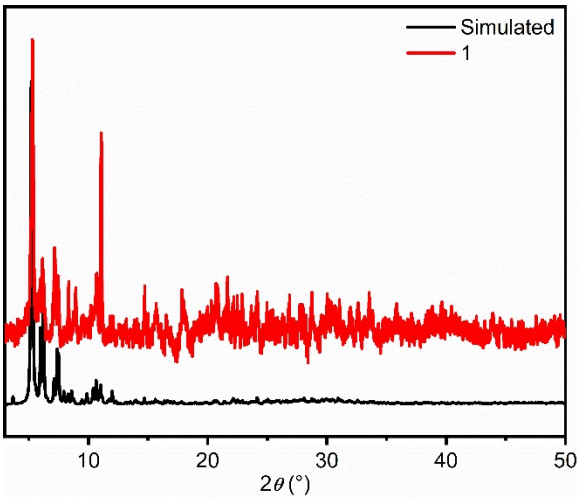

Fig. S1 The experimental and the simulated PXRD patterns of **1**.

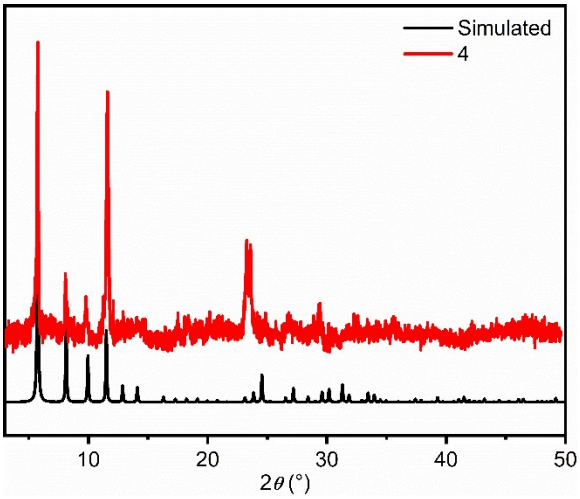

Fig. S2 The experimental and the simulated PXRD patterns of **4**.

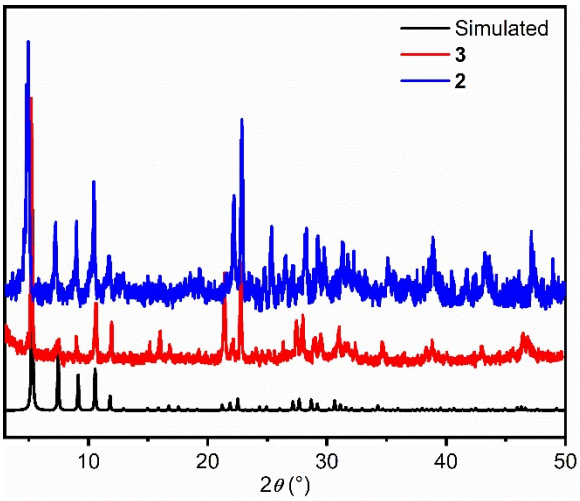

Fig. S3 The experimental and the simulated PXRD patterns of **2** and **3**.

Section S5: Photographs of Crystals

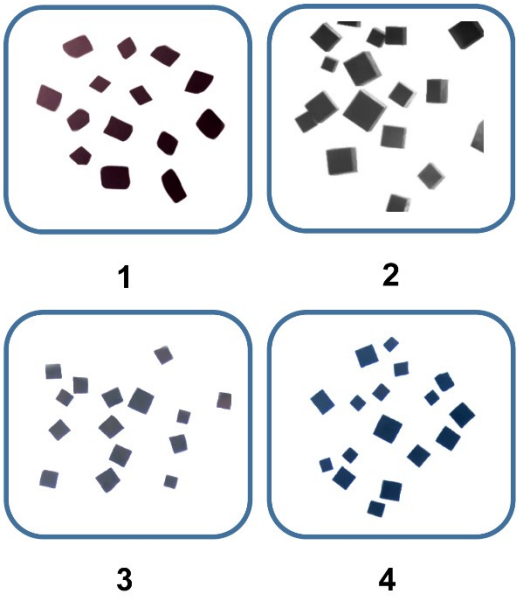

Fig. S4 The photographs of the crystals (**1-4**).

Section S6: Scanning Electron Microscopy (SEM)

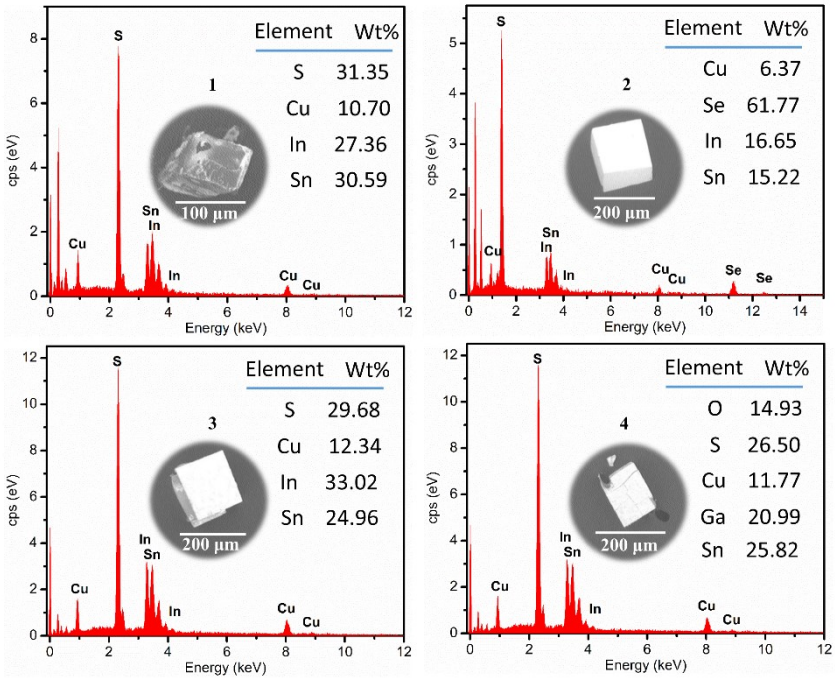

Fig. S5 The SEM images (inset) and the energy dispersive spectroscopy (EDS) of the P2 clusters.

Section S7: Thermogravimetric Analysis (TGA)

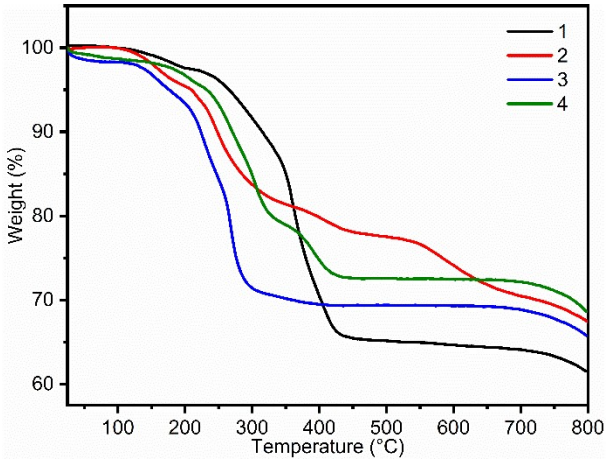

Fig. S6 The TG curves of P2 clusters.

Section S8: Fourier Transformed-Infrared (FT-IR) Spectroscopy

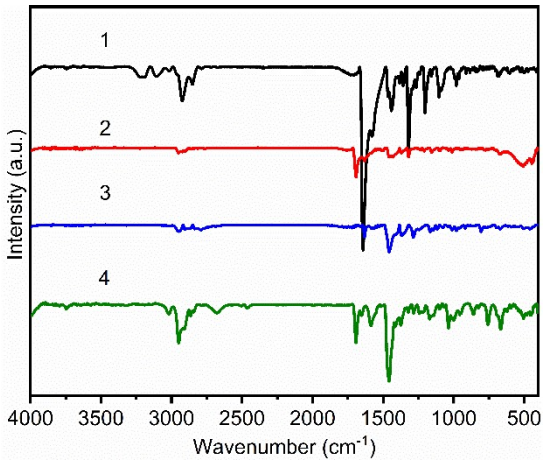

Fig. S7 The FT-IR spectra of P2 clusters.

Section S9: Dispersion experiments of P2 clusters

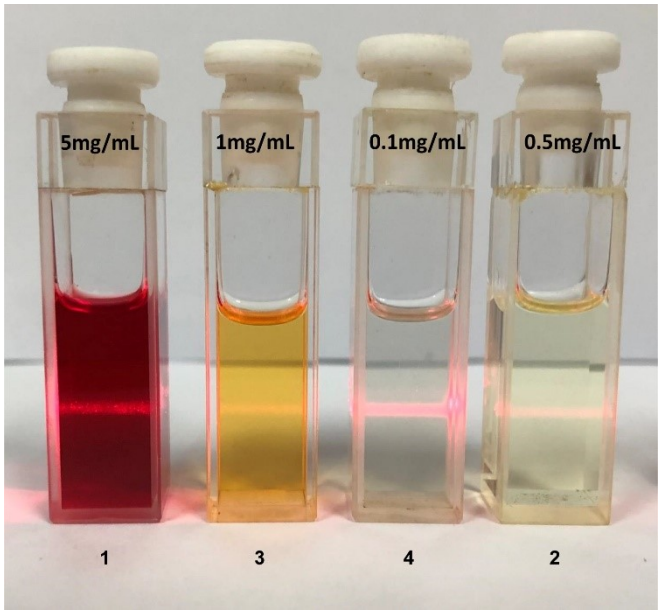

Fig. S8 The optical photos of dispersions of P2 clusters in the solution (**1** and **3** in DMSO, **4** in piperidine, **2** in pyridine).

Section S10: Transmission Electron Microscope (TEM)

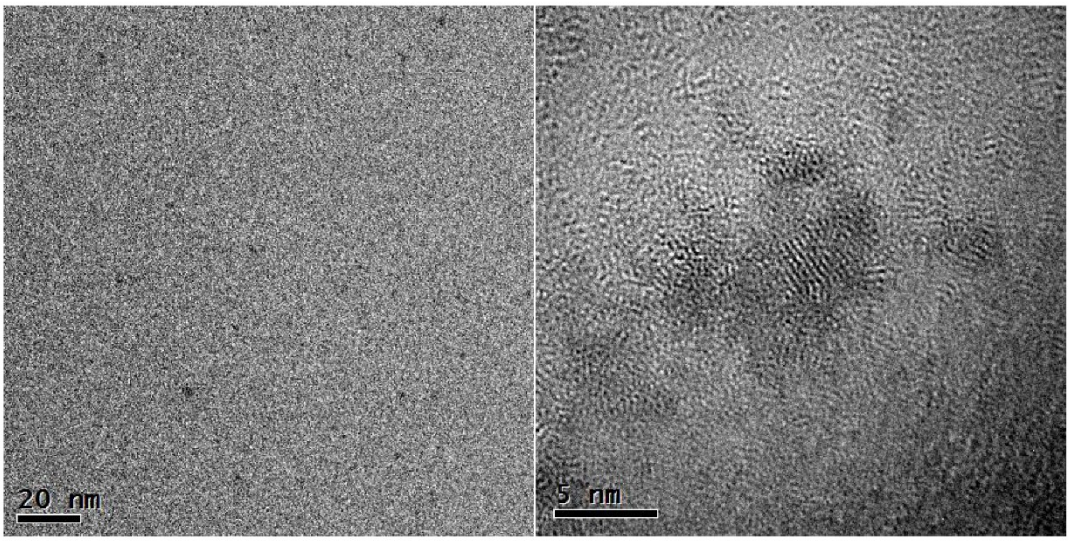

Fig. S9 The TEM (left) and HR-TEM (right) images of the **1** after dispersion DMSO.

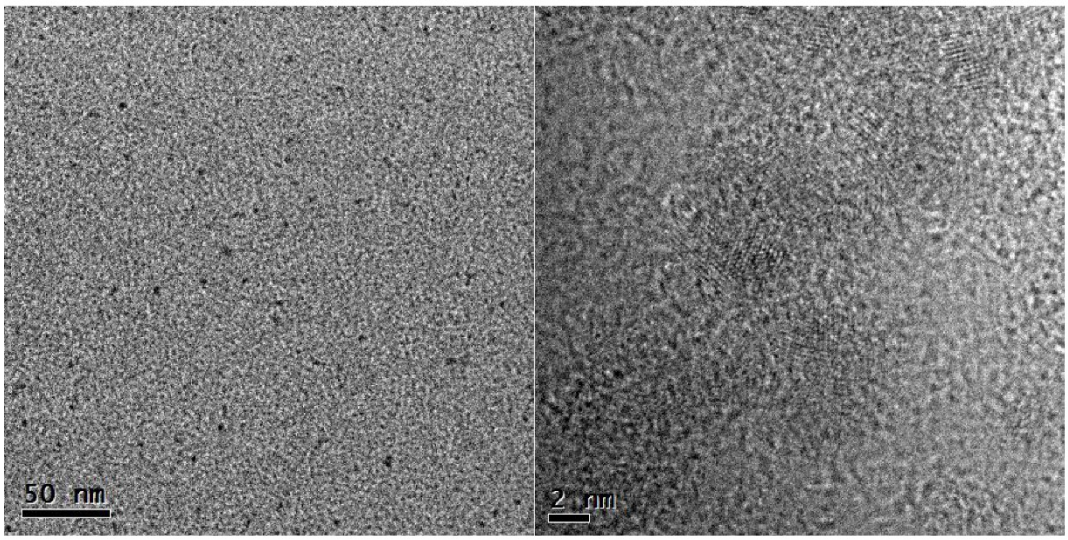

Fig. S10 The TEM (left) and HR-TEM (right) images of the **2** after dispersion in pyridine.

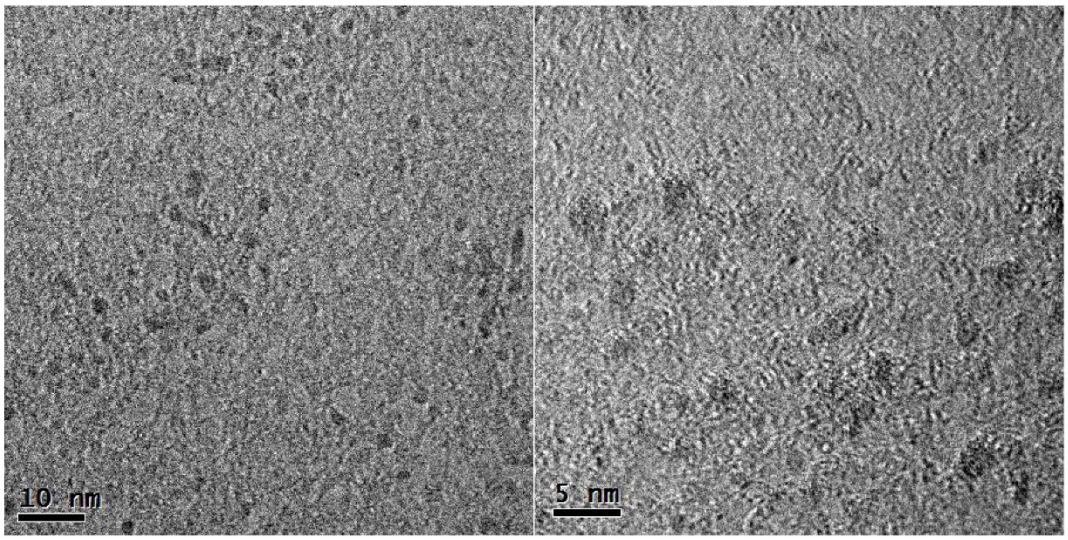

Fig. S11 The TEM (left) and HR-TEM (right) images of the **3** after dispersion in DMSO.

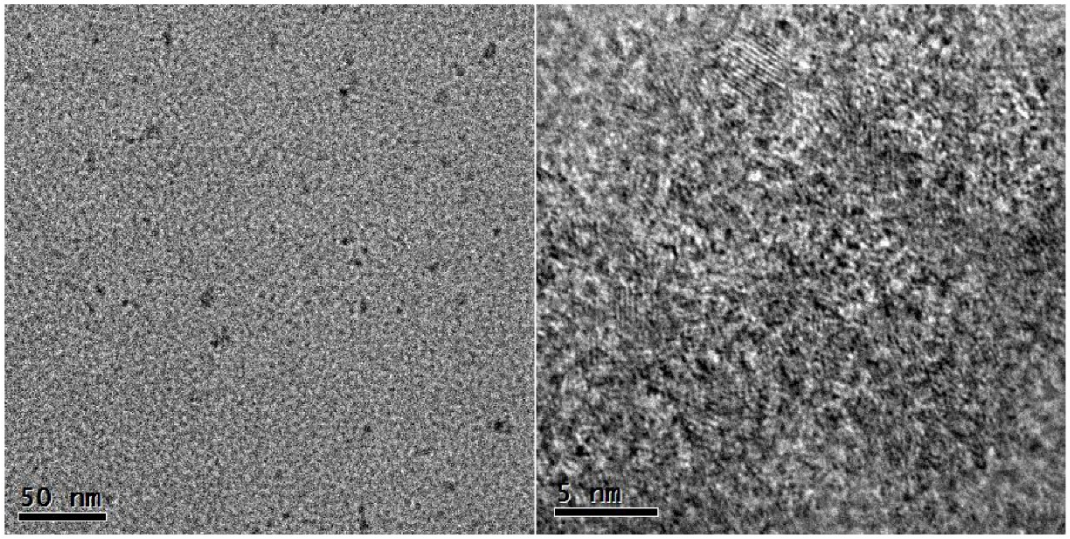

Fig. S12 The TEM (left) and HR-TEM (right) images of the **4** after dispersion in piperidine.

Section S11: Solid Ultraviolet-Visible (UV-Vis) Spectroscopy

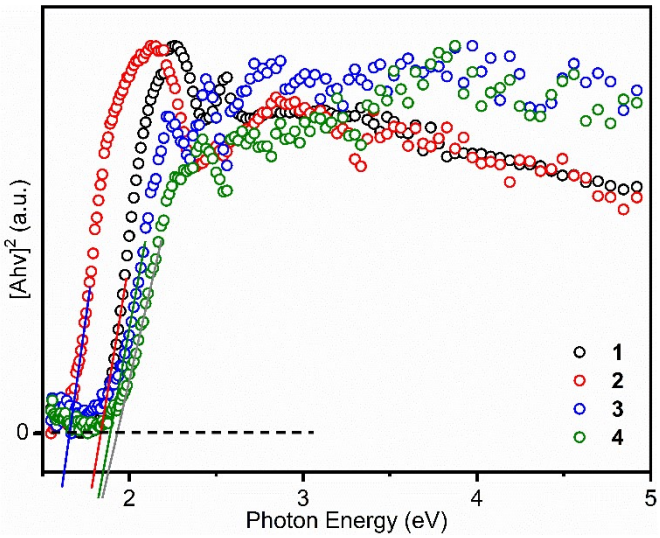

Fig. S13 The tauc plots of P2 clusters.

Section S12: Dynamic Light Scattering (DLS) Experiments

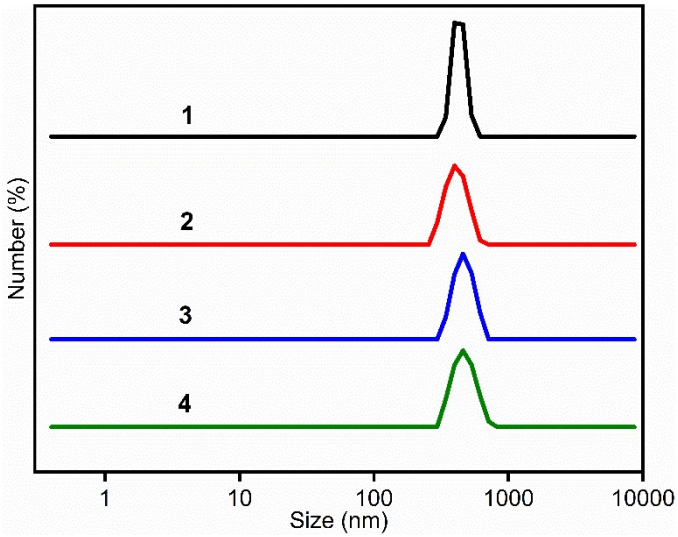

Fig. S14 The DLS number-weighted diameters of dispersion of P2 clusters in ethanol with same linear transmittance of 0.6.

Section S13: Electrochemical impedance spectroscopy (EIS) measurements

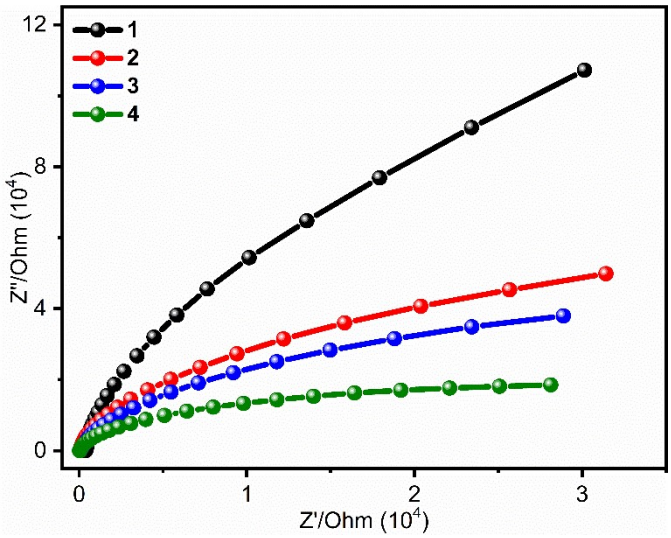

Fig. S15 EIS curves of P2 clusters with laser irradiation.

Section S14 : Z-Scan measurements

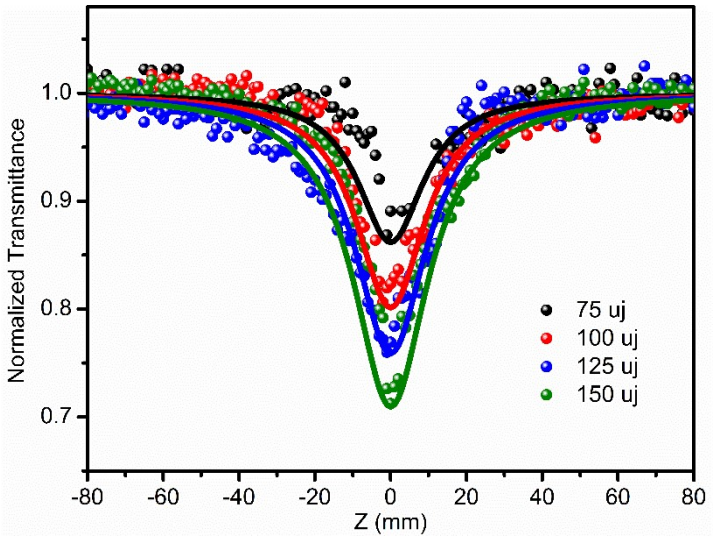

Fig. S16 The NLO behavior of the **3** disperse in ethanol at the different incident pulse energy.

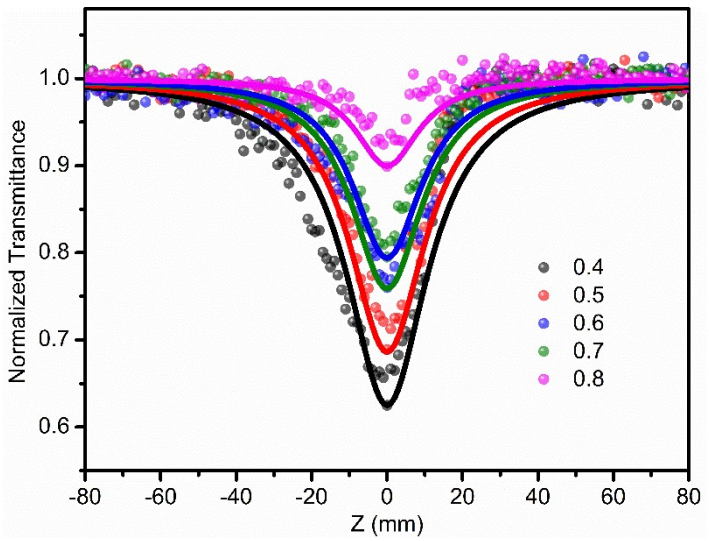

Fig. S17 The nonlinear response of **3** disperse in ethanol with different transmittance from 0.4 to 0.8 at the incident pulse energy of 125 μJ.

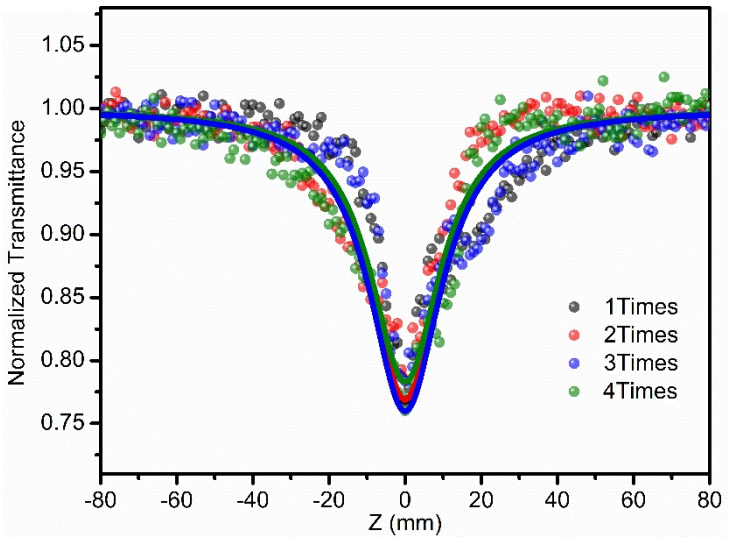

Fig. S18 The open-aperture Z-scan results at 532 nm for **3** disperse in ethanol (the solution is tested at the same point).

Section S14: References

(1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009,** *42*, 339-341.
(2) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - Olex2 dissected. *Acta Cryst* **2015,** ***A****71*, 59-75.
(3) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst* **2015,** ***C****71*, 3-8.
(4) van der Sluis, P.; Spek, A. L. BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions. *Acta Cryst* **1990,** ***A****46*, 194-201.