Supplementary Information (SI) for Dalton Transactions.

Partial Congener Substitution Induced Wide Band Gap Witnessed by the Diamond-Like Chalcogenide $ZnHg_2P_2S_8$ and Its Second-Order Nonlinear Optical Properties

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1. Experimental methods

X-ray Diffraction Analysis

Single-crystal X-ray diffraction (SCXRD) data were collected on a Rigaku XtaLAB Synergy four-circle diffractometer with Mo-Kα radiation (λ = 0.71073 Å) for $ZnHg_2P_2S_8$. The structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. In the crystal structure models, $Zn1^{2+}$ and $Hg1^{2+}$ cations co-occupy the same atomic site. Crystal date is shown in **Table 1**. The atomic coordinates, equivalent displacement parameters, bond valence sums (BVS), and the important bond lengths and angles are shown in **Tables S1 and S2**.

Powder X-ray Diffraction

The powder X-ray diffraction pattern of the as-obtained polycrystalline powders was performed at room temperature on a Bruker D8 Focus diffractometer with Cu Kα (λ = 1.5418 Å) radiation. The scanning step width of 0.03° and a fixed counting time of 0.1 s/step were applied to record the patterns in the 2θ range of 10–70°.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX)

A Hitachi S-4800 SEM equipped with an Oxford INCAx-act EDX system was applied to semiquantitatively characterize the element type and content of the as-obtained single crystals. The accelerating voltage and probe current were set to 20 keV and 70 mA, respectively. The spectra were analyzed using Oxford Instruments AZtec software.

Diffuse reflectance spectroscopy

The diffuse reflectance spectrum was recorded at room temperature on a Cary 7000 UV-vis-NIR spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range of 200–2500 nm.

A compacted pellet of polytetrafluoroethylene (PTFE) was used as a 100% reflectance standard. The absorption spectrum was calculated from the reflection spectrum by the Kubelka-Munk function.[1]

Thermal Analysis

The differential scanning calorimeter (DSC) analysis was performed on the Labsys EVO TG/DTA/DSC 1600 °C (SETARAM) thermal analyzer. Polycrystalline samples $ZnHg_2P_2S_8$ were sealed within small fused-silica tubes, which were evacuated to 10^{-3} Pa and heated from room temperature to 973 K at the rate of 5 K/min.

Powder SHG Measurement

The SHG response of $ZnHg_2P_2S_8$ was measured by means of the Kurtz-Perry method[2] employing a 2090 nm laser as fundamental light generated by a Q-switched Ho: Tm: Cr: YAG laser (1 Hz, 50 ns). The polycrystalline powder of $ZnHg_2P_2S_8$ was thoroughly ground and sieved into several desired particle size ranges of 20–41, 41–74, 74–105, 105–150, 150–200, and 200–250 μm. These samples were clamped by two glass microscope slides and secured with tape in a 1 mm-thick aluminum holder. Commercial microcrystalline $AgGaS_2$ samples of the same particle size range were selected as the references.

2. Figures and Tables

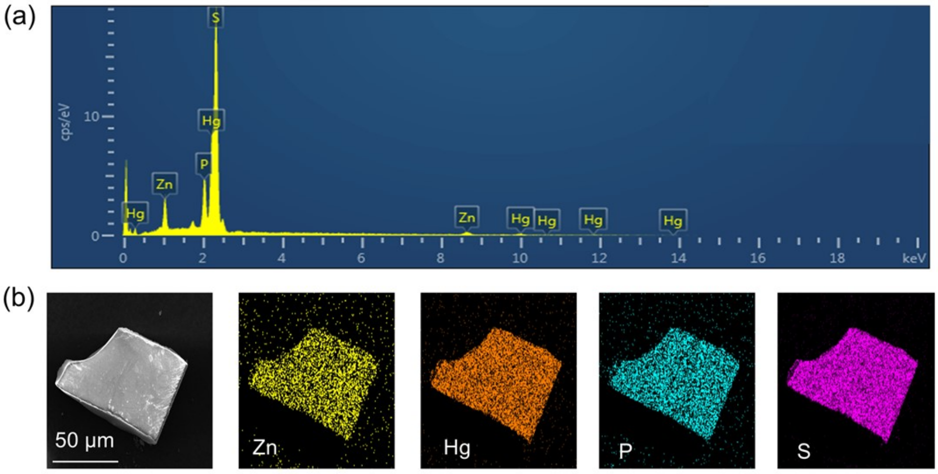

Fig. S1. (a) Elemental analysis of $ZnHg_2P_2S_8$ by EDX spectroscopy; (b) Scanning electron microscopy (SEM) image and elemental distribution of $ZnHg_2P_2S_8$.

Table S1 Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for $ZnHg_2P_2S_8$.

Atom	Wyckoff position	x	y	z	U_{eq} (Å^2) [a]	Occ.	BVS
M1 = Zn1/Hg1	8b	0.75425(5)	0.51023(6)	0.70034(6)	0.0237(2)	0.5/0.5	2.16
Hg2	4a	0.5	0	0.29848(11)	0.0299(2)	1.0	2.05
P1	8b	0.63038(13)	0.2677(3)	0.4670(3)	0.0129(5)	1.0	5.20
S1	8b	0.6258(2)	0.4908(3)	0.5747(3)	0.0198(6)	1.0	−2.10
S2	8b	0.61668(16)	0.0595(3)	0.5888(3)	0.0224(6)	1.0	−2.02
S3	8b	0.74313(14)	0.2643(3)	0.3632(3)	0.0179(6)	1.0	−2.12
S4	8b	5323.4(16)	2863(3)	3295(3)	20.5(5)	1.0	−2.14

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2 Selected band distances (Å) and band angles (°) for ZnHg$_2$P$_2$S$_8$.

M1–S1^{1}	2.400(3)	Hg2–S4	2.380(3)
M1–S2^{4}	2.377(3)	Hg2–S4^{3}	2.380(3)
M1–S3^{5}	2.478(3)	P1–S1	2.049(4)
M1–S3^{6}	2.536(3)	P1–S2	2.026(3)
Hg2–S1^{1}	2.904(3)	P1–S3	2.074(3)
Hg2–S1^{2}	2.904(3)	P1–S4	2.043(3)
S1—M1—S3^{4}	105.76(9)	S4—Hg2—S1^{2}	87.22(9)
S1—M1—S3^{5}	104.59(9)	S4—Hg2—S1^{1}	102.53(8)
S2^{6}—M1—S1	125.54(9)	S4—Hg2—S4^{3}	166.30(15)
S2^{6}—M1—S3^{4}	100.49(9)	S1—P1—S3	105.38(15)
S2^{6}—M1—S3^{5}	112.11(9)	S2—P1—S1	117.07(15)
S3^{5}—M1—S3^{4}	106.90(11)	S2—P1—S3	109.85(14)
S1^{1}—Hg2—S1^{2}	90.20(12)	S2—P1—S4	108.26(15)
S4^{3}—Hg2—S1^{1}	87.22(9)	S4—P1—S1	101.77(15)
S4^{3}—Hg2—S1^{2}	102.53(8)	S4—P1—S3	114.53(15)

Symmetry codes: ^{1}1−X,1/2−Y,−1/2+Z; ^{2}+X,−1/2+Y,−1/2+Z; ^{3}1−X,−Y,+Z; ^{4}+X,1/2+Y,1/2+Z; ^{5}3/2−X,+Y,1/2+Z; ^{6}3/2−X,1/2+Y,+Z

Reference

1. E. L. Simmons, *Appl. Opt.*, 1975, **14**, 1380-1386.
2. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798-3813.