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Electronic Supplementary Information (ESI)

γ-$P_4S_3I_2$: A New Metal-free Infrared Second-order Nonlinear Optical Crystal Designed by Polymorphism Strategy

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Table of Contents

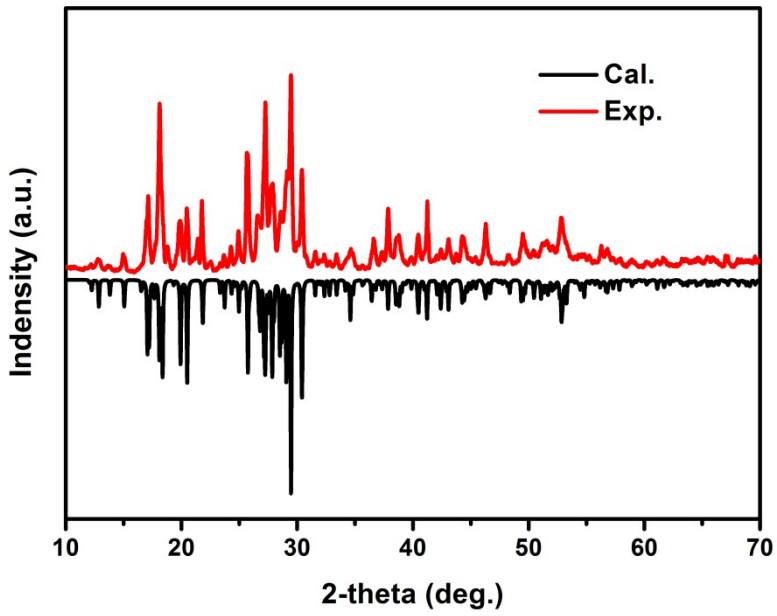

Figure S1 Calculated and experimental powder X-ray diffraction patterns of γ-$P_4S_3I_2$.

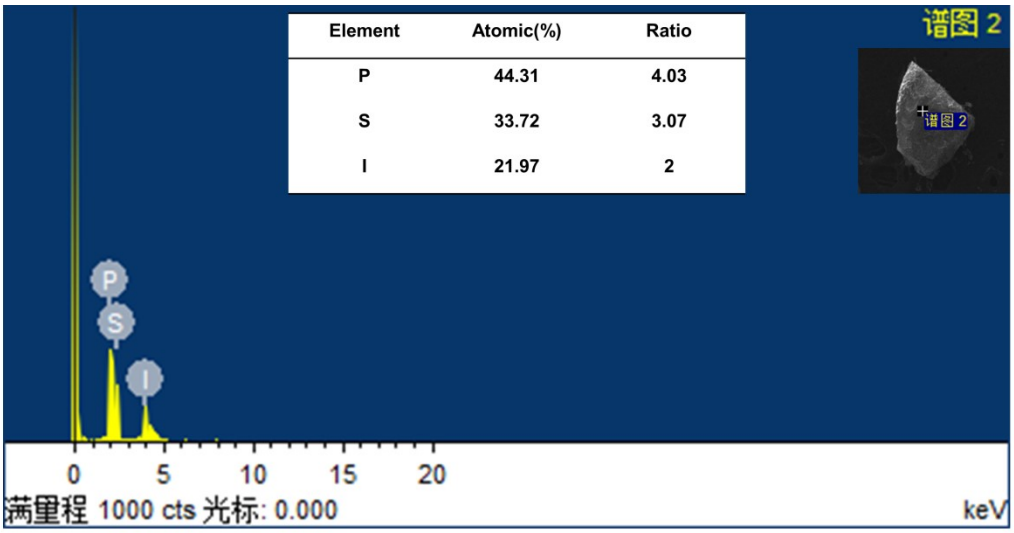

Figure S2 Energy-dispersive X-ray Spectroscopy analysis of γ-$P_4S_3I_2$.

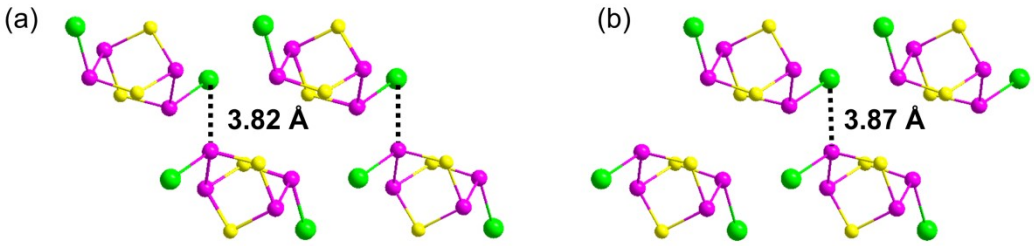

Figure S3 The experimental I···P distance in the $(P_4S_3I_2)_n$ (n=4) molecular cluster of γ-$P_4S_3I_2$ (a) and α-$P_4S_3I_2$ (b).

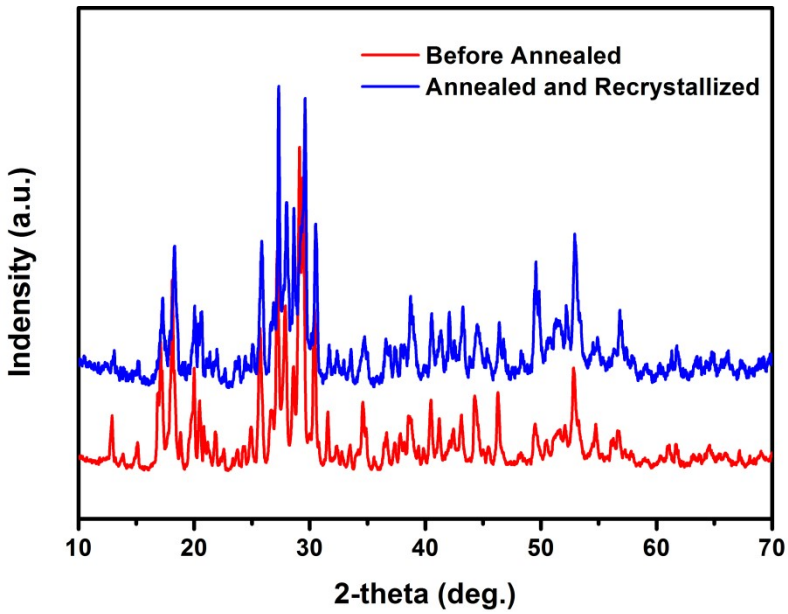

Figure S4 Powder X-ray diffraction patterns of γ-$P_4S_3I_2$ before annealed and γ-$P_4S_3I_2$ annealed at 125°C and recrystallized in CS_2.

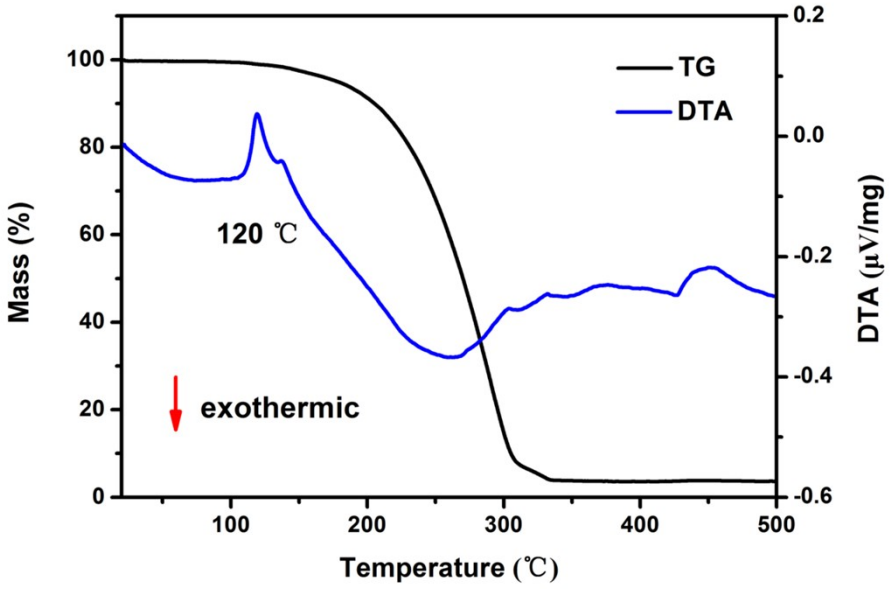

Figure S5 TG-DTA curves of γ-$P_4S_3I_2$.

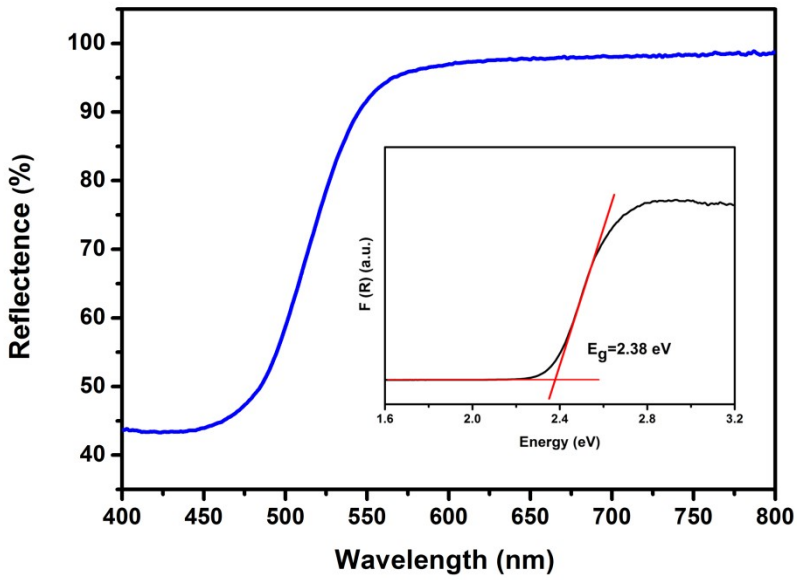

Figure S6 UV-vis-NIR diffuse reflectance spectra of γ-$P_4S_3I_2$. Inset shows the derivation of band gap.

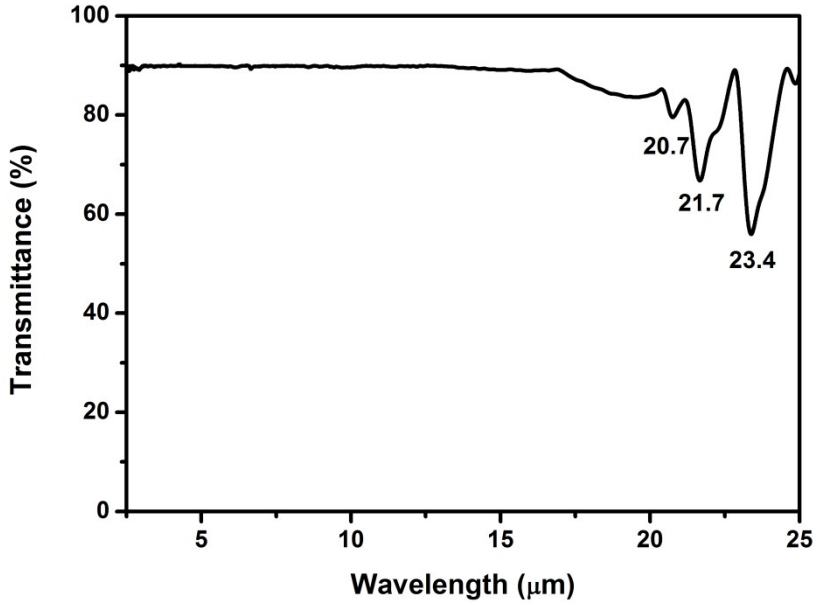

Figure S7 FT-IR transmittance spectra of γ-$P_4S_3I_2$.

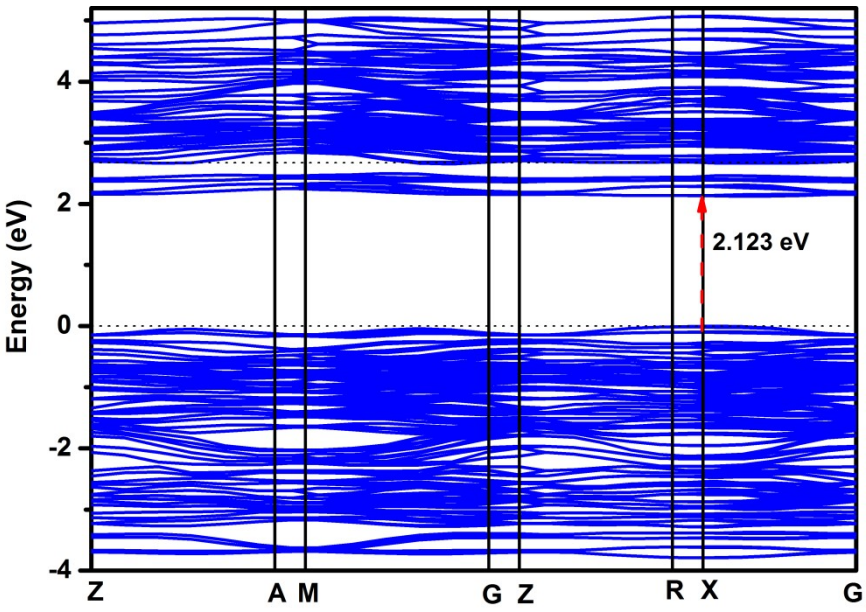

Figure S8 Calculated band structure of γ-$P_4S_3I_2$.

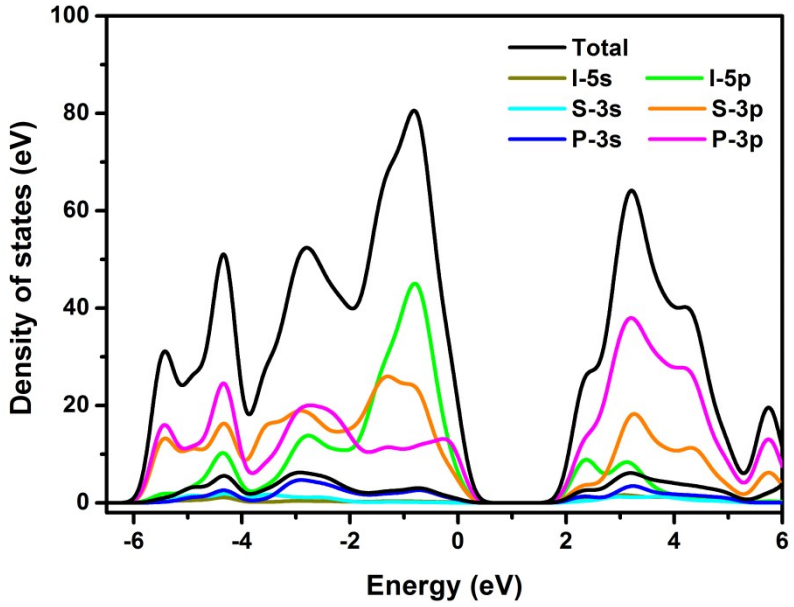

Figure S9 Partial density of states (PDOS) of γ-$P_4S_3I_2$.

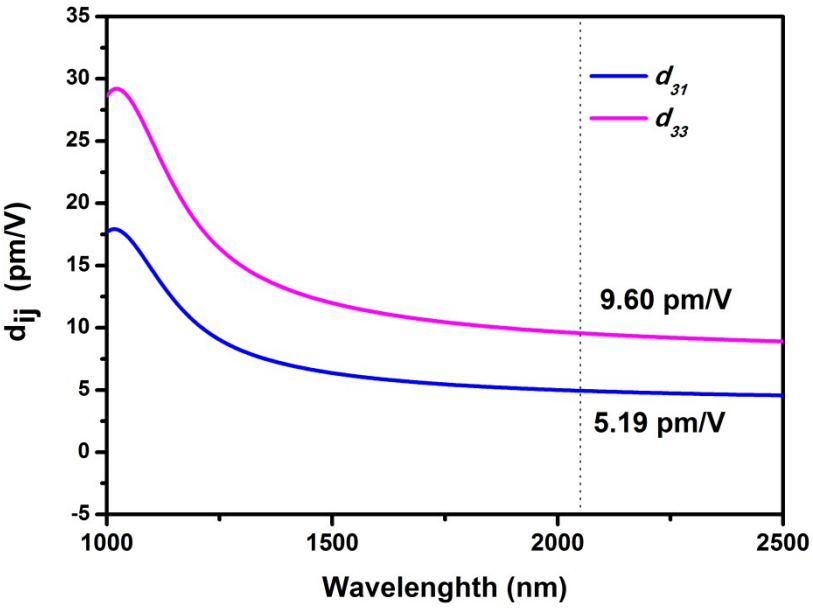

Figure S10 Calculated frequency-dependent coefficients of γ-$P_4S_3I_2$.

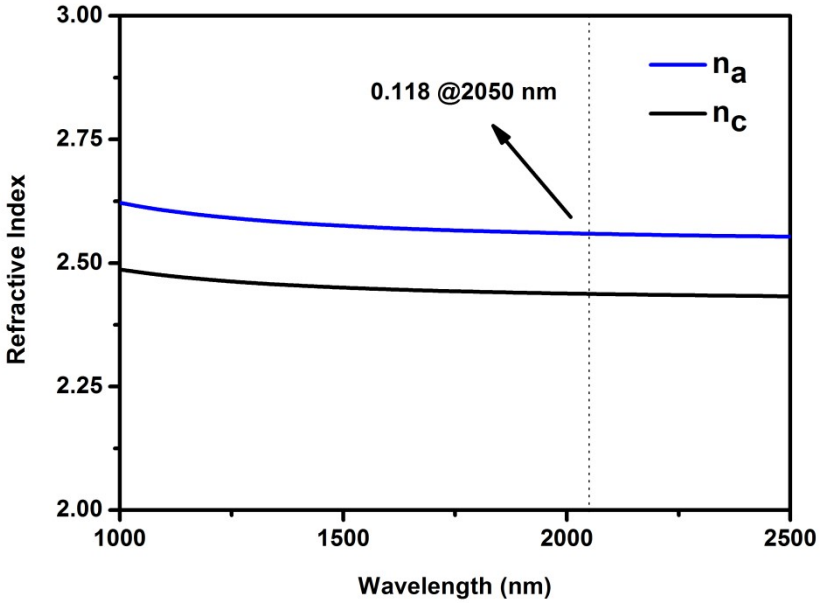

Figure S11 The calculated refractive index dispersion curves of *γ*-$P_4S_3I_2$.

Table S1. Crystal Data and Structure Refinement Details of *γ*-$P_4S_3I_2$ [a,b].

Formula	$P_4S_3I_2$
Formula weight (amu)	473.86
Temperature (K)	293(2)
λ (Å)	0.71073
Crystal system	Tetragonal
Space group	P 4_3
a (Å)	7.3415(2)
b (Å)	7.3415(2)
c (Å)	39.1942(19)
α /°	90
β /°	90
γ /°	90
V (Å^3)	2112.47(15)
Z	8

ρ_{calc} (Mg/m^3)	2.980
μ (mm^{-1})	7.080
Crystal size (mm^3)	0.01 x 0.01 x 0.01
θ range (deg)	2.078 to 30.739
Index ranges	-9<=h<=7
	-8<=k<=8
	-42<=l<=54
F(000)	1712
Reflections collected/unique	8811 / 4583
R_{int}	0.0293
R/wR (I>2 σ(I))	R_1= 0.0381, wR_2= 0.0808
R/wR (all data)	R_1= 0.0553, wR_2= 0.0851
GOF on F^2	1.003

[a]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. [b]$wR_2(F_o^2)=[\sum wF_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for *γ*-$P_4S_3I_2$

Atom	x	y	z	U(eq)
I(1)	-491(1)	-3776(1)	5758(1)	50(1)
I(2)	5192(1)	11550(1)	4246(1)	50(1)
I(3)	6683(1)	3001(1)	5247(1)	51(1)
I(4)	12046(2)	4485(2)	4787(1)	60(1)
S(1)	6330(5)	6853(5)	4098(1)	45(1)
S(2)	4199(5)	-2732(5)	5911(1)	45(1)
S(3)	8466(5)	8469(5)	4770(1)	47(1)
S(4)	2690(5)	-502(5)	5237(1)	48(1)
S(5)	11235(5)	7751(6)	4123(1)	55(1)
S(6)	3410(6)	2182(5)	5900(1)	55(1)
P(1)	7368(5)	9449(5)	3968(1)	39(1)
P(2)	5109(5)	-1361(5)	5462(1)	42(1)
P(3)	1638(5)	-1622(5)	6036(1)	42(1)
P(4)	5936(5)	1096(5)	5750(1)	42(1)
P(5)	9557(5)	9806(5)	4346(1)	45(1)
P(6)	1350(5)	587(5)	5660(1)	48(1)
P(7)	7686(5)	6003(5)	4549(1)	45(1)
P(8)	10207(5)	5213(5)	4277(1)	46(1)

Table S3. Selected bond lengths [Å] and angles [deg.] for *γ*-$P_4S_3I_2$

I(1)-P(3)	2.477(4)	P(4)-S(6)-P(6)	107.08(19)
I(2)-P(1)	2.473(3)	S(1)-P(1)-I(2)	102.94(16)
I(3)-P(4)	2.480(3)	S(1)-P(1)-P(5)	102.06(18)
I(4)-P(8)	2.471(3)	P(5)-P(1)-I(2)	95.79(16)
S(1)-P(1)	2.114(5)	S(2)-P(2)-P(4)	92.85(18)
S(1)-P(7)	2.123(5)	S(4)-P(2)-S(2)	103.06(19)
S(2)-P(2)	2.135(5)	S(4)-P(2)-P(4)	101.8(2)
S(2)-P(3)	2.106(5)	S(2)-P(3)-I(1)	102.37(17)
S(3)-P(5)	2.089(5)	S(2)-P(3)-P(6)	102.45(19)
S(3)-P(7)	2.088(5)	P(6)-P(3)-I(1)	96.60(16)
S(4)-P(2)	2.082(5)	S(6)-P(4)-I(3)	101.75(17)
S(4)-P(6)	2.087(5)	S(6)-P(4)-P(2)	102.12(19)
S(5)-P(5)	2.136(5)	P(2)-P(4)-I(3)	96.58(15)
S(5)-P(8)	2.100(5)	S(3)-P(5)-S(5)	102.4(2)
S(6)-P(4)	2.102(5)	S(3)-P(5)-P(1)	101.5(2)
S(6)-P(6)	2.132(6)	S(5)-P(5)-P(1)	93.4(2)
P(1)-P(5)	2.202(5)	S(4)-P(6)-S(6)	103.1(2)
P(2)-P(4)	2.212(5)	S(4)-P(6)-P(3)	101.8(2)
P(3)-P(6)	2.202(5)	S(6)-P(6)-P(3)	92.30(19)
P(7)-P(8)	2.211(5)	S(1)-P(7)-P(8)	93.98(19)
P(1)-S(1)-P(7)	107.19(19)	S(3)-P(7)-S(1)	102.7(2)
P(3)-S(2)-P(2)	106.73(19)	S(3)-P(7)-P(8)	101.4(2)
P(7)-S(3)-P(5)	100.45(19)	S(5)-P(8)-I(4)	103.25(18)
P(2)-S(4)-P(6)	100.41(19)	S(5)-P(8)-P(7)	101.9(2)
P(8)-S(5)-P(5)	107.5(2)	P(7)-P(8)-I(4)	97.19(15)

Table S4. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *γ*-$P_4S_3I_2$.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + 2hka^*b^* U_{12} + \ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	43(1)	51(1)	56(1)	2(1)	-4(1)	-12(1)
I(2)	49(1)	45(1)	58(1)	-7(1)	-4(1)	11(1)
I(3)	55(1)	50(1)	49(1)	8(1)	-2(1)	-16(1)
I(4)	60(1)	57(1)	61(1)	1(1)	-9(1)	21(1)
S(1)	38(2)	42(2)	56(2)	-3(1)	-5(1)	-3(2)
S(2)	37(2)	40(2)	60(2)	14(1)	1(1)	2(2)
S(3)	51(2)	57(2)	34(2)	-4(1)	0(1)	9(2)

S(4)	52(2)	54(2)	38(2)	4(1)	-8(2)	-8(2)
S(5)	39(2)	60(2)	66(2)	16(2)	17(2)	6(2)
S(6)	61(2)	41(2)	63(2)	-13(2)	12(2)	-6(2)
P(1)	42(2)	37(2)	38(2)	3(1)	2(1)	6(2)
P(2)	39(2)	39(2)	47(2)	-2(1)	8(1)	3(2)
P(3)	38(2)	40(2)	48(2)	-4(1)	3(1)	-4(2)
P(4)	43(2)	43(2)	39(2)	4(1)	-4(1)	-6(2)
P(5)	39(2)	38(2)	60(2)	3(2)	-3(2)	-5(2)
P(6)	35(2)	42(2)	67(2)	5(2)	-2(2)	6(2)
P(7)	41(2)	41(2)	53(2)	11(1)	6(1)	-1(2)
P(8)	50(2)	41(2)	47(2)	-4(1)	-2(2)	11(2)

Table S5. Powder Laser Damage Threshold (LDT) Measurements

Compounds	Energy (mJ)	Spot area (cm^2)	Pulse width (ns)	LDT (MW/cm^2)
γ-$P_4S_3I_2$	1.7	0.0153938	10	11.97286
$AgGaS_2$	0.6	0.0153938	10	4.25241