Supporting Information

The first polyanion substitution-driven centrosymmetric-to-noncentrosymmetric structural transformation realizing excellent nonlinear optical supramolecule $[Cd_4P_2][CdBr_4]$

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Contents

Figures and Tables

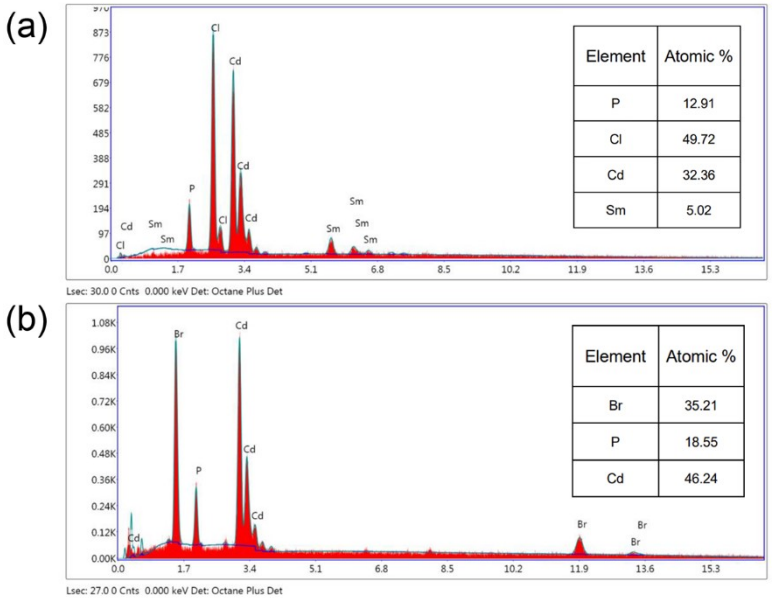

Fig. S1 EDS of **1** (a) and **2** (b).

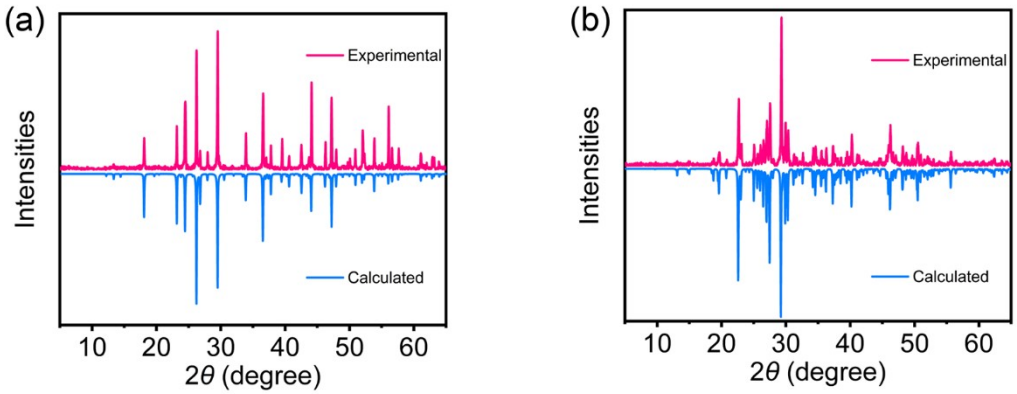

Fig. S2 The powder XRD patterns of **1** (a) and **2** (b).

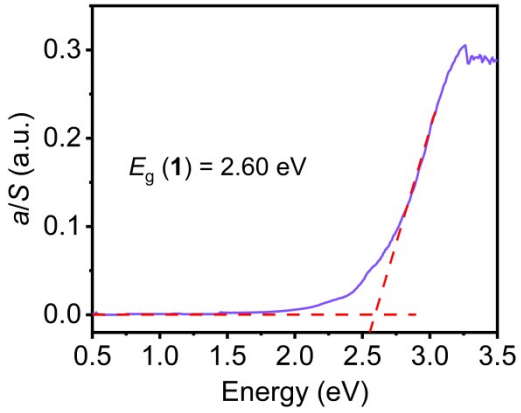

Fig. S3 Band gap of **1**.

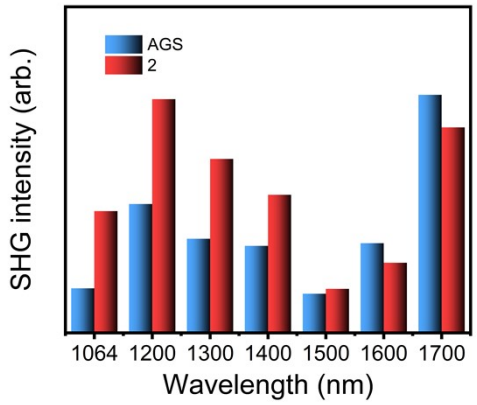

Fig. S4 The SHG responses of **2** at broadband wavelength 1064 to 1700 nm.

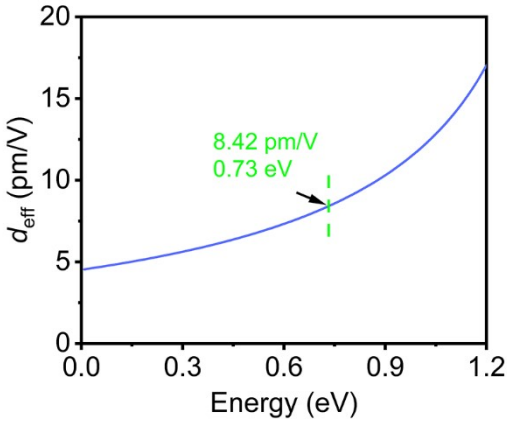

Fig. S5 Effective NLO coefficient for **2**.

Table S1. Crystallographic data and structure refinement parameters for **1** and **2**.

Empirical formula	$[Cd_5P_2][SmCl_6]Cl$ (**1**)	$[Cd_4P_2][CdBr_4]$ (**2**)
CCDC	2235035	2235036
Fw	1022.50	943.58
Temperature (K)	293(2)	293(2)
Space group	*P*-3	$Pna2_1$
a (Å)	13.350(4)	12.1965(8)
b (Å)	13.350(4)	13.6691(10)
c (Å)	7.308(4)	7.7077(7)
V (Å^3)	1128.0(9)	1284.99(17)
Z	3	4
D_{calcd} (g·cm^{-3})	4.516	4.877
μ (mm^{-1})	12.199	20.769
GOF on F^2	1.005	0.999
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0611	0.0451
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.1643	0.1320
$R_1{}^a$ (all data)	0.0786	0.0479
$wR_2{}^b$ (all data)	0.1810	0.1338
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	2.38/-2.27	2.21/-1.47

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR = (\Sigma(w(F_o{}^2-F_c{}^2)^2)/\Sigma(w(F_o{}^2)^2))^{1/2}$.

Table S2. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **1** and **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

1				
Atom	*x*	*y*	*z*	*Ueq*
Sm1	3333	6667	647(3)	24.4(5)
Sm1B	3333	6667	9648(18)	25(3)
Sm2	0	0	610(3)	27.7(7)
Cl3	4998(3)	3294(3)	1713(5)	32.8(9)
Cl4	3378(4)	4785(4)	1751(6)	48.8(11)
Cl5	1801(4)	1709(4)	1742(6)	47.7(11)
Cl6	3333	6667	4412(15)	97(4)
Cl7	0	0	4410(20)	101(8)
Cd8	160.6(12)	3400.0(12)	377.9(16)	53.1(5)
Cd9	5000	0	5000	77.6(9)
Cd10	3336.0(18)	1645.3(13)	4902(2)	75.0(7)
P11	60(3)	3363(3)	3699(5)	21.3(8)
2				
Atom	*x*	*y*	*z*	*Ueq*
Cd1	7768.6(17)	7500.1(13)	9879(3)	36.3(5)
Cd2	7480.7(13)	9134.4(19)	5069(4)	48.9(6)
Cd3	5095(2)	5464.1(17)	8023(3)	48.2(6)
Cd4	9501.3(17)	5023.7(17)	6538(3)	45.5(6)

Cd5	9927(2)	2413.5(16)	8939(4)	45.8(7)
Br6	9983.2(18)	7725(2)	10001(4)	40.1(6)
Br7	7282(2)	9280.0(18)	9179(4)	36.6(6)
Br8	7491.2(17)	6277(2)	7411(4)	37.2(6)
Br9	7492.7(19)	6862(2)	2943(4)	40.9(7)
P10	9458(4)	9158(4)	5089(8)	24.0(11)
P11	9433(5)	4133(4)	9370(8)	25.8(12)

Table S3. Bond Lengths for **1** and **2**.

1			
Bond	**Length/Å**	**Bond**	**Length/Å**
Sm1−Cl3×3	2.798(4)	Sm2−Cl7	2.775(1)
Sm1−Cl4×3	2.668(4)	P11−Cd8	2.430(4)
Sm1B−Cl3×3	2.417(6)	P11−Cd9	2.430(4)
Sm1B−Cl4×3	2.971(8)	P11−Cd9	2.422(3)
Sm2−Cl5×3	2.908(5)	P11−Cd10	2.420(3)
Sm2−Cl5×3	2.487(5)	P11−Cd10	2.421(3)
2			
Bond	**Length/Å**	**Bond**	**Length/Å**
Cd1−Br6	2.720(3)	Cd5−Br6	3.043(4)
Cd1−Br7	2.562(3)	P10−Cd3	2.454(6)
Cd1−Br8	2.555(3)	P10−Cd3	2.446(7)
Cd1−Br9	2.540(4)	P10−Cd5	2.441(6)
Cd3−Br6	2.910(4)	P11−Cd2	2.407(6)
Cd4−Br7	3.012(4)	P11−Cd4	2.444(6)
Cd4−Br8	3.066(3)		

Table S4. Calculation of dipole moment for tetrahedrons and net dipole moment for a unit cell.

Polar unit	Dipole moment (Debye)		
	x-component	*y*-component	*z*-component
$CdBr_4$	±14.46	±1.78	(−0.47) × 4
$P10Cd_4$	±9.9	±0.10	(2.20) × 4
$P11Cd_4$	±8.99	±2.73	(4.93) ×4
Net dipole moment (a unit cell)	0	0	26.64

Table S5. The LIDTs of compound **2** and AGS.

Compounds	Damage energy (mJ)	Spot area (cm^2)	τ_p (ns)	Damage threshold [$MW \cdot cm^{-2}$]
2	4.0	0.05	10	33.3
AGS	1.2	0.05	10	10.0