Supporting Information

"Old dog, new tricks": the lone pair effect inducing divergent optical responses in lead cyanurates containing π-bonds

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Experimental procedures

Synthesis. All chemicals containing $Pb(OH)_2$ (Macklin, ≥98%), $Cd(OH)_2$ (Macklin, 98.5%) and $H_3C_3N_3O_3$ (Aladdin, 98%)were used without further purification and their dissolution in deionized water took place in air.

Single crystals of I and II were synthesized by hydrothermal methods. The mixture of $Pb(OH)_2$, $H_3C_3N_3O_3$ with a molar ratio of 3:2 in H_2O (8.0 mL) was sealed in an autoclave with a Teflon liner (23 mL) and heated at 130 °C for 12 hours, which was slowly cooled to room temperature at a rate of 2°C/h. Under the same conditions, II was synthesized from $Pb(OH)_2$, $Cd(OH)_2$, $H_3C_3N_3O_3$ with a molar ratio of 2:1:2 in H_2O (8.0 mL) Colorless and transparent crystals with regular shapes were obtained after washing with deionized water and ethanol.

Powder X-ray diffraction. The powder X-ray diffraction (PXRD) data of the target samples were successfully collected on Bruker D8 Focus diffractometer equipped with Cu Kα radiation (λ=1.5418 Å) in the 2θ range of 5-70° at room temperature.

UV–vis–NIR diffuse reflectance spectrum. The UV-vis-NIR diffuse reflectance spectra were measured in the wavelength range from 200 nm to 2000 nm with $BaSO_4$ as a reference material by Cary 7000 UV-vis-NIR universal measurement spectrophotometer under an integrating sphere.

IR spectrum. FTIR spectrum of I was collected on a Varian Excalibur 3100 spectrometer in the 400 - 4000 cm^{-1} range. I and KBr samples were mixed thoroughly with mass ratio about 1:100, respectively.

Thermal analysis. Thermal gravimetric analysis (TGA) were carried out on NETZSCH STA 409 CD thermal analyzer at a temperature range of 100-550 °C and 100-600 °C for I and II respectively with a heating rate of 10 K/min in nitrogen atmosphere.

Single crystal structure determination. The single-crystal X-ray diffraction data was gathered on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ= 0.71073 Å) and Saturn CCD detector at 293 K.

The intensity data, data reduction and cell refinement were captured by the CrystalClear program. The crystal structures were settled by the direct method with grogram SHELXS-97 and further refined by full matrix least squares on F^2 by SHELXL-97 programs. The structure was confirmed by using the ADDSYM algorithm from the program PLATON with no higher symmetry discovered. The crystallographic data are given in Table S1 - 3.

Computational methods.

Notably, a similar chemical formula $Pb_3O_2(O_3C_3N_3H_2)_2$ with non-centrosymmetric *Cc* space group has been reported by Meyer's group in 2015.[1] We checked these two structures carefully and identity the refined structure in this work is indeed accurate. So, all following calculations are based on this experimental structure without any optimizations. The theoretical calculations for isostructural $Pb_3(HC_3N_3O_3)_2(OH)_2$ and $Pb_2Cd(HC_3N_3O_3)_2(OH)_2$ were performed by *ab initio* density functional theory[2] on basis of CASTEP module.[3] In early reports, this method has been applied on H-free metal cyanurates as well as hydro-cyanurates successfully.[4-12] The exchange–correlation (XC) functional was modeled by the generalized gradient density approximation (GGA)[13] and the norm-conserving pseudopotentials[14] were applied for all elements. In this model, Pb $6s^26p^2$, Cd $5s^24p^64d^{10}$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$ and H 1*s* electrons were modeled as the outer valence electrons, respectively. The kinetic energy cutoff of 900 eV and dense *k*-point meshes[15] (2×4×2) in the first Brillouin zone were chosen to guarantee the sufficient calculation accuracy.

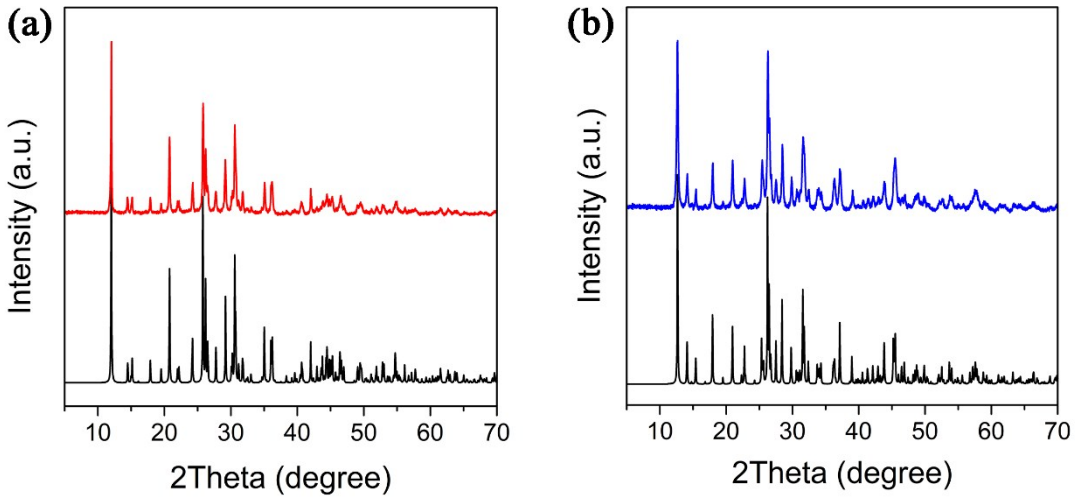

Figure S1. Experimental powder XRD spectra of (a) I and (b) II

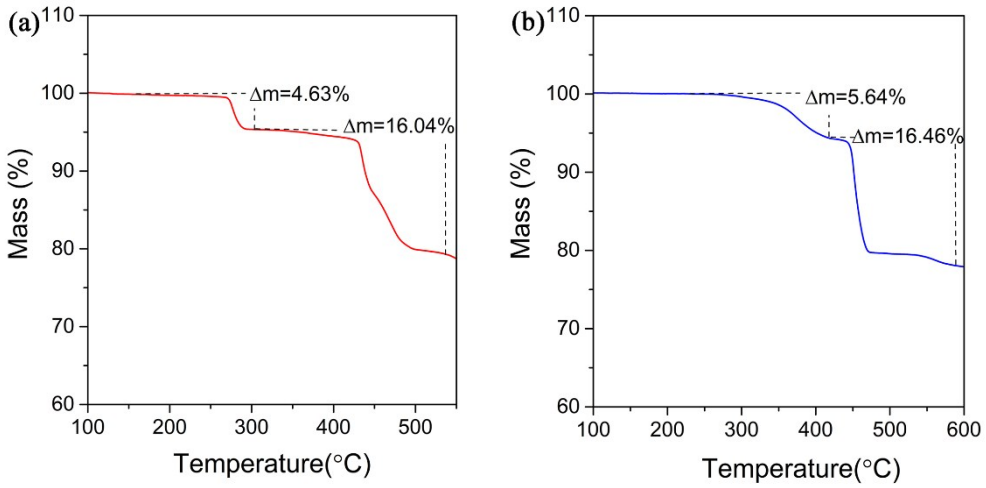

Figure S2. The TG curves for (a) I and (b) II

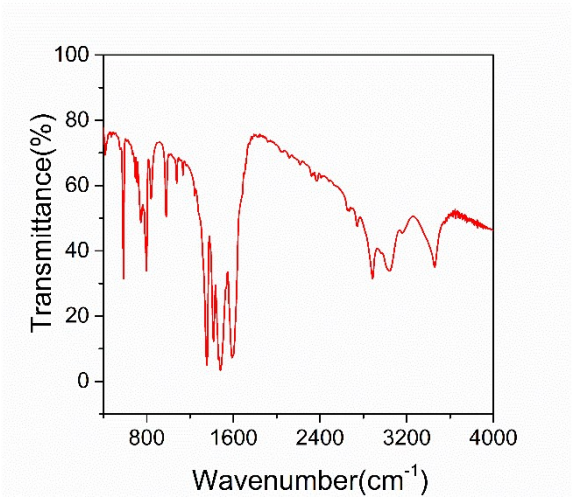

Figure S3. The IR spectrum of I

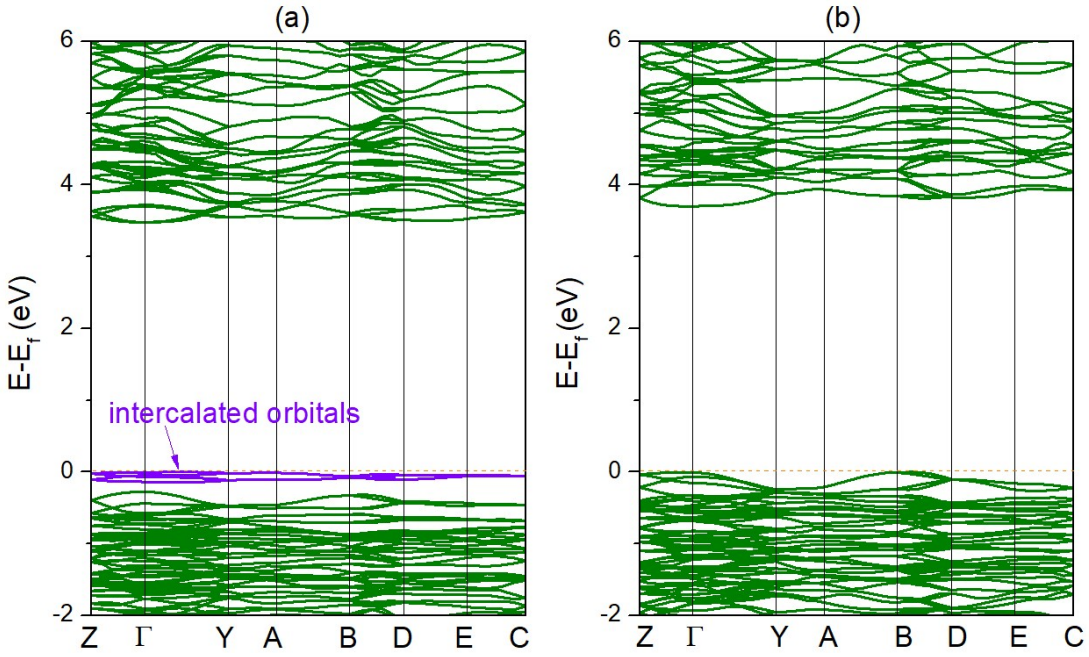

Figure S4. Calculated band structure calculated by PBE functional, (a) I and (b) II

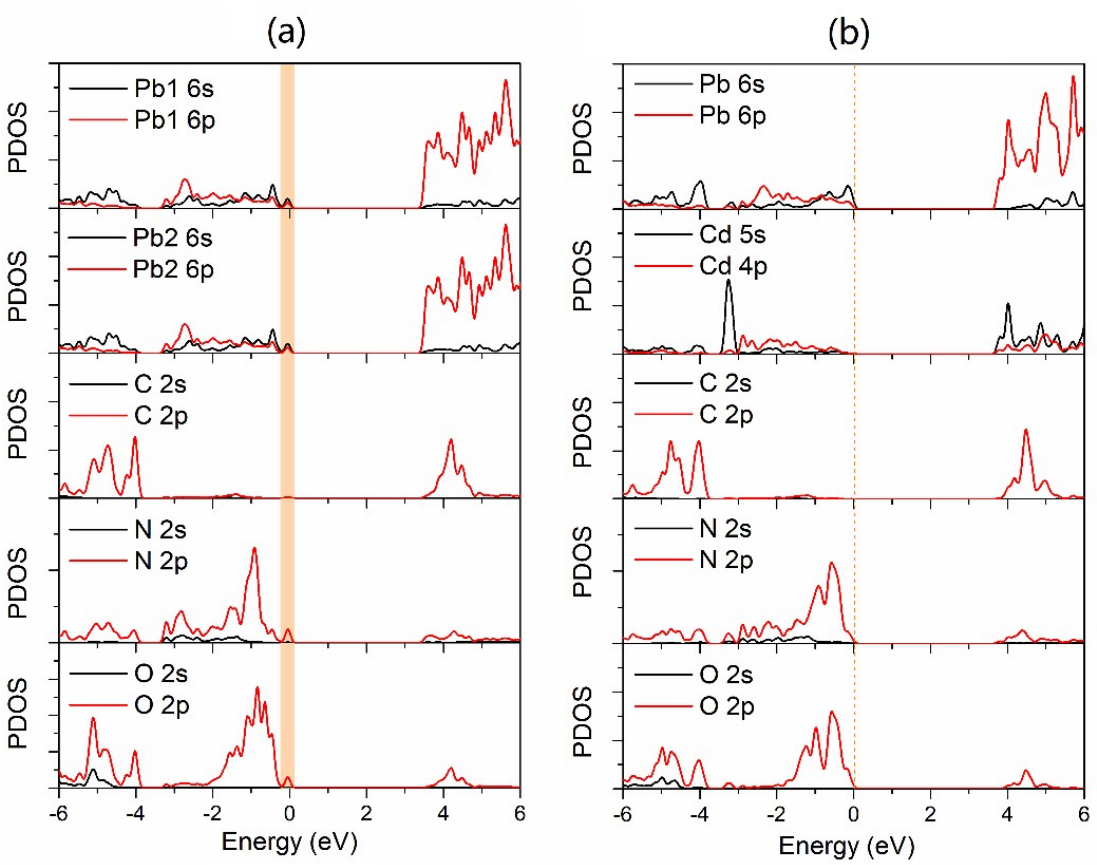

Figure S5. The partial density of states projected constituent atoms of (a) I and (b) II. The contribution from hydroxyl molecule was omitted for simplification.

Table S1. Crystal data and structure refinements for I and II

Chemical formula	I	II
Formula weight	909.72	814.93
Temperature/K	293	293
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	16.6034 (11)	15.9504 (12)
b/Å	6.7166 (3)	7.0252 (4)
c/Å	12.4132 (6)	12.0267 (8)
α/°	90	90
β/°	117.563 (6)	118.914 (7)
γ/°	90	90
Volume/Å^3	1227.19 (11)	1179.66 (14)
Z	4	4
R_{int}	0.035	0.035
ρ_{calc} g/cm^3	4.924	4.589
μ/mm^{-1}	41.12	30.32
F(000)	1568	1432
Goof on F^2	1.111	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0194, wR_2 = 0.0448	R_1 = 0.0181, wR_2 = 0.0448
Final R indexes [all data]	R_1 = 0.0203, wR_2 = 0.0451	R_1 = 0.0197, wR_2 = 0.0455

[a]$R_1 = \sum \| |F_O| - |F_C| \| / \sum |F_O|$ and $wR_2 = \left[\sum \left[w\left(F_O^2 - F_C^2\right)^2\right] / \sum \left[w\left(F_O^2\right)^2\right]\right]^{\frac{1}{2}}$ for $F_O^2 > 2\sigma\left(F_C^2\right)$

Table S2. Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) for I and II

I				
	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	1.062308 (12)	1.20157 (3)	0.609544 (16)	0.01761 (9)
Pb2	1.0000	0.72291 (4)	0.7500	0.01499 (9)
C1	0.6705 (3)	0.4975 (6)	0.4455 (4)	0.0141 (9)
C2	0.7567 (3)	0.6057 (7)	0.6470 (4)	0.0141 (9)
C3	0.8338 (3)	0.4994 (6)	0.5420 (4)	0.0144 (9)
N1	0.6741 (3)	0.5747 (6)	0.5476 (3)	0.0152 (8)
N2	0.7515 (2)	0.4602 (6)	0.4444 (3)	0.0164 (8)
N3	0.8364 (3)	0.5631 (6)	0.6457 (3)	0.0178 (8)
O1	1.0423 (2)	0.8541 (5)	0.5949 (3)	0.0172 (7)
O2	0.7564 (3)	0.6793 (5)	0.7391 (3)	0.0247 (8)
O3	0.9043 (2)	0.4808 (5)	0.5300 (3)	0.0220 (7)
O4	0.5977 (2)	0.4607 (5)	0.3521 (3)	0.0211 (7)
II				
	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	1.055927 (15)	1.20519 (3)	0.607963 (18)	0.01807 (11)
Cd1	1.0000	0.75964 (8)	0.7500	0.01442 (14)
C1	0.6796 (4)	0.4848 (7)	0.4601 (5)	0.0167 (11)
C2	0.7726 (4)	0.6294 (8)	0.6594 (5)	0.0183 (11)
C3	0.8509 (4)	0.5198 (8)	0.5485 (5)	0.0189 (11)
N1	0.6852 (3)	0.5750 (7)	0.5626 (4)	0.0187 (10)
N2	0.7629 (3)	0.4541 (7)	0.4563 (4)	0.0191 (10)
N3	0.8550 (3)	0.6037 (7)	0.6523 (4)	0.0196 (10)
O1	1.0410 (3)	0.8666 (6)	0.6050 (3)	0.0166 (8)
O2	0.7742 (3)	0.7108 (6)	0.7513 (4)	0.0244 (9)
O3	0.9212 (3)	0.5042 (6)	0.5329 (4)	0.0246 (9)

O4	0.6037 (3)	0.4306 (6)	0.3697 (3)	0.0209 (8)

Table S3. Select bond lengths (Å) and angles (degree) for I and II

		I	
Pb1-O1^{i}	2.349 (3)	C1-N2	1.374 (5)
Pb1-O1	2.353 (4)	C2-O2	1.247 (5)
Pb1-N1^{ii}	2.467 (3)	C2-N3	1.361 (6)
Pb2-O1^{iii}	2.495 (3)	C2-N1	1.372 (6)
Pb2-O1	2.495 (3)	C3-O3	1.253 (6)
Pb2-O4^{iv}	2.617 (3)	C3-N3	1.338 (6)
Pb2-O4^{v}	2.617 (3)	C3-N2	1.369 (6)
Pb2-N3	2.637 (4)	C1-O4	1.253 (6)
Pb2-N3^{iii}	2.637 (4)	C1-N1	1.345 (6)
O4-C1-N1	123.4 (4)	O3-C3-N3	122.0 (4)
O4-C1-N2	119.0 (4)	O3-C3-N2	118.7 (4)
N1-C1-N2	117.6 (4)	N3-C3-N2	119.2 (4)
O2-C2-N3	120.7 (4)	C1-N1-C2	119.8 (4)
O2-C2-N1	117.3 (4)	C3-N2-C1	122.4 (4)
N3-C2—N1	122.0 (4)	C3-N3-C2	118.7 (4)
		II	
Pb1-O1^{i}	2.319 (4)	C1-N1	1.350 (7)
Pb1-O1	2.389 (4)	C1-N2	1.369 (7)
Pb1-N1^{ii}	2.545 (4)	C2-O2.	1.234 (7)
Cd1-O1^{iii}	2.266 (3)	C2-N3	1.369 (7)
Cd1-O1	2.266 (3)	C2-N1	1.369 (7)
Cd1-N3	2.302 (5)	C3-O3	1.228 (6)
Cd1-N3^{iii}	2.302 (5)	C3-N3	1.353 (7)
C1-O4	1.232 (7)	C3-N2	1.381 (8)
O4-C1-N1	123.6 (5)	O3-C3-N3	122.7 (5)
O4-C1-N2	118.5 (5)	O3-C3-N2	119.7 (5)
N1-C1-N2	117.9 (5)	N3-C3-N2	117.6 (5)
O2-C2-N3	120.8 (5)	C1-N1-C2	119.9 (5)
O2-C2-N1	117.5 (5)	C1-N2-C3	123.1 (4)
N3-C2-N1	121.6 (5)	C3-N3-C2	119.7 (5)

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