Supplementary information

Targeted regulation and optimization of multifunctional phase transition materials by novel void occupancy engineering

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Experimental Section

Synthesis

For the synthesis of [TMEA][Cd(SCN)$_3$], ethyltrimethylammonium chloride was prepared from iodide using Ag$_2$CO$_3$ and hydrochloric acid in a stoichiometric ratio. Then, ethyl trimethyl ammonium chloride (5 mmol), cadmium nitrate tetrahydrate (5 mmol) and potassium thiocyanate (15 mmol) were added to the solution mixture including water, methanol and acetonitrile in the ratio of 1:1:1 under stirring at room temperature, and the clarified solution was filtered through filter paper and left to evaporate slowly at room temperature for several days to obtain colorless and transparent rod-shaped crystals. As for the synthesis of [DEDMA][Cd(SCN)$_3$], [TEMA][Cd(SCN)$_3$], and [TEA][Cd(SCN)$_3$], except that [DEDMA][Cd(SCN)$_3$] requires the preparation of diethyl dimethylammonium chloride by using hydrochloric acid and diethyl dimethyl ammonium hydroxide in a stoichiometric manner, the other synthesis steps are similar to that of [TMEA][Cd(SCN)$_3$]. A few days later, colorless transparent rod-shaped single crystals of [DEDMA][Cd(SCN)$_3$], [TEMA][Cd(SCN)$_3$], and [TEA][Cd(SCN)$_3$] were collected (Fig. S1).

Detailed methods of measurements

Single-crystal X-ray diffraction. Single crystal X-ray diffraction data for [TMEA][Cd(SCN)$_3$], [DEDMA][Cd(SCN)$_3$], [TEMA][Cd(SCN)$_3$], and [TEA][Cd(SCN)$_3$] were obtained using a Rigaku Saturn 724 diffractometer using Mo-Kα Radiation (λ= 0.71073 Å). Data collection, cell refinement, and data restoration are performed using Rigaku Crystal Clear 1.3.5. The crystal structure is solved using a direct method, and then refined by full-matrix least-squares methods based on F^2 with the SHELXLTL software package. All non-hydrogen atoms are refined in an anisotropic manner, and the positions of all hydrogen atoms are generated geometrically. Import the generated CIF file into DIAMOND to draw the corresponding asymmetric cell diagram and stack diagram, and calculate the selected bond distances and angles through Mercury. Table S1-S4 and S8-S11 summarize the data collection and bond length and bond angle of these crystals. These X-ray crystal structures have been stored at the Cambridge Crystallography Data Center (storage number CCDC 2265083-2265089) and are available free of charge from CCDC at www.ccdc.cam.ac.uk/getstructures.

Differential Scanning Calorimetry (DSC). DSC measurement was performed on powder sample of [TMEA][Cd(SCN)$_3$], [DEDMA][Cd(SCN)$_3$], [TEMA][Cd(SCN)$_3$], and [TEA][Cd(SCN)$_3$] by a

NETZSCH DSC 214 Polyma instrument. The sample was placed in aluminum crucible under nitrogen at atmospheric pressure. The experiment was conducted under nitrogen and atmospheric pressure, with heating and cooling rates of 20 K·min^{-1}.

Dielectric Measurements. The powder is pressed into thin sheets, and the copper wire and sample are made into electrodes using silver glue. Dielectric measurements were performed at different temperatures on the Tonghui TH2828A instrument.

Second Harmonic Generation (SHG). Temperature-varying SHG of [TEA][Cd(SCN)$_3$] were performed using a low-divergence, unexpanded laser beam (pulsed Nd: YAG with a wavelength of 1064 nm) with a pulse duration of 10 ns at a temperature range of 330-390 K.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) measurements were performed at room temperature on a Rigaku D/MAX 2000 PC X-ray diffractometer. The diffraction pattern is recorded at 2θ between 5-50° within the range, the step size is 0.02°.

Density Functional Theory (DFT) Calculations. The Density functional theory were carried out with the Vienna Ab Initio Simulation Package (VASP)[1]. The projector-augmented wave method (PAW)[2] and Perdew-Burke-Ernzerhof (PBE)[3] functional were used to describe the electron-ion and the exchange-correlation interactions respectively. The energy barrier for the rotation of cations were calculated based on crystal structures of the [DEDMA][Cd(SCN)$_3$], [TEMA][Cd(SCN)$_3$] and [TEA][Cd(SCN)$_3$]. The optimization by structural relaxation is required for [TEMA][Cd(SCN)$_3$] and [TEA][Cd(SCN)$_3$]. In this study, the Brillouin area was divided by the sampled grids of 2*2*1 Monkhorst-Pack mesh of k-points for [DEDMA][Cd(SCN)$_3$] and [TEA][Cd(SCN)$_3$]. A k-point grid with 2*1*2 Monkhorst-Pack mesh was chosen for the 4ethy. A cutoff energy of 500 eV was adopted for all simulations. In the self-consistent calculation, the energy convergence criteria was set to 10^{-5}eV, and the geometric configuration was completely relaxed until the force on each atom reached 0.02eV/Å. A cutoff energy of 500 eV was adopted for all simulations.
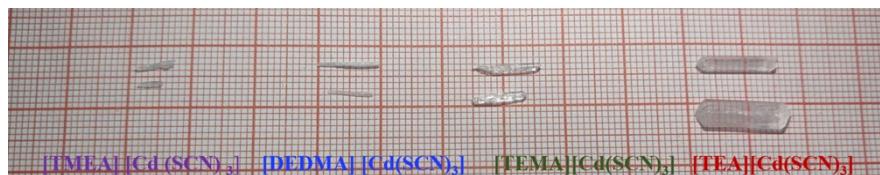
**Fig. S1** Obtained crystal photos of four compounds.
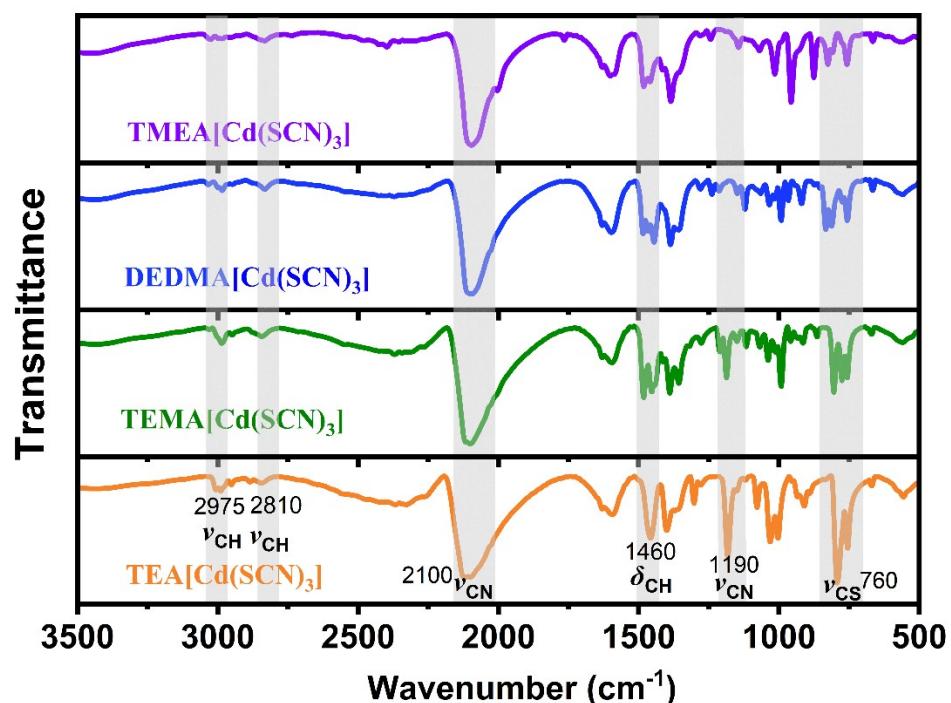
**Fig. S2** Infrared (IR) spectrums of four compounds.
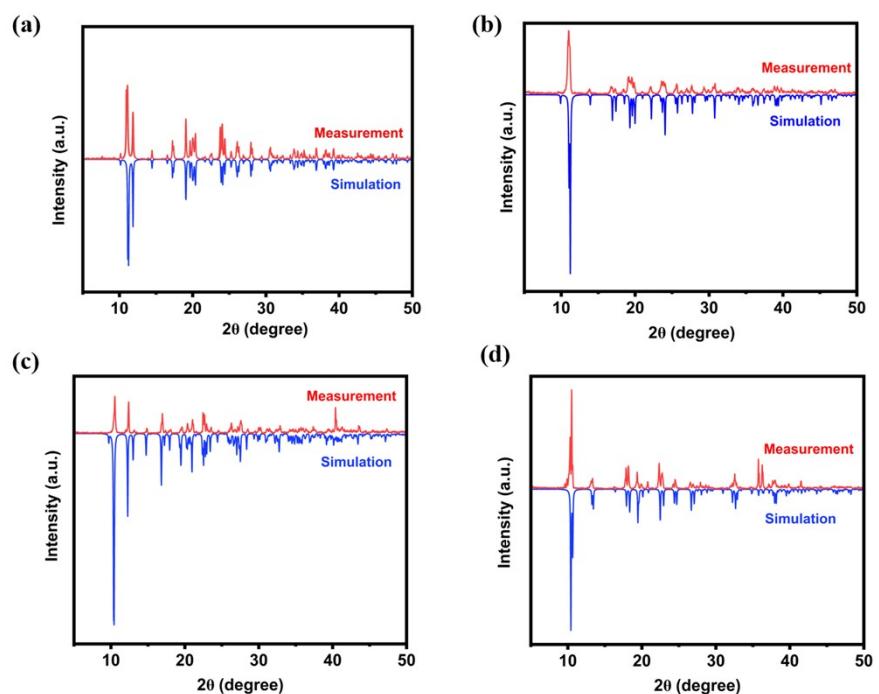
Fig. S3 The measured and simulated PXRD patterns of four compounds match well, verifying the

phase purity of the compounds [TMEA][Cd(SCN)$_3$] (a), [DEDMA][Cd(SCN)$_3$] (b), [TEMA][Cd(SCN)$_3$] (c) and [TEA][Cd(SCN)$_3$] (d).
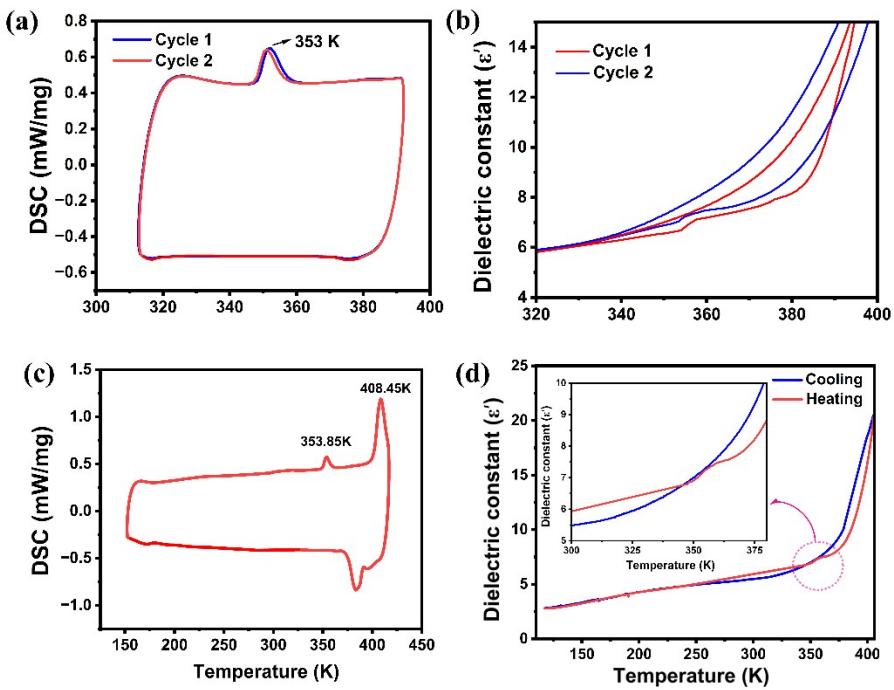
Fig. S4 (a), (b) DSC and dielectric measurements of [TMEA][Cd(SCN)$_3$] under two consecutive cycles (c) DSC curve of polycrystalline sample of [TMEA][Cd(SCN)$_3$] during heating-cooling cycle (150-408 K). [TMEA][Cd(SCN)$_3$] has a melting point of 408 K and exhibits a melting-solidification peak. (b) The temperature dependent dielectric constant (ε') of [TMEA][Cd(SCN)$_3$] was measured during a heating-cooling cycle (120-403 K). An irreversible dielectric switching occurs at about 354 K.
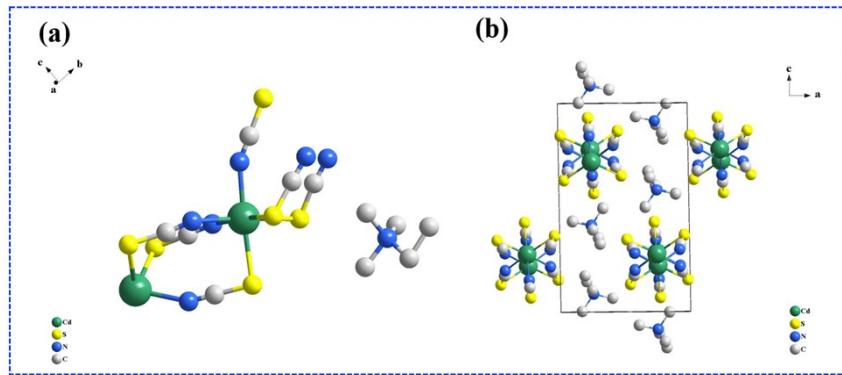
Fig. S5 (a) Molecular structure of [TMEA][Cd(SCN)$_3$] at 298 K (containing [Cd(SCN)$_3$]$^-$ chains and [DEDMA]$^+$ cations). (b) crystal packing structures of [TMEA][Cd(SCN)$_3$] at 298 K.
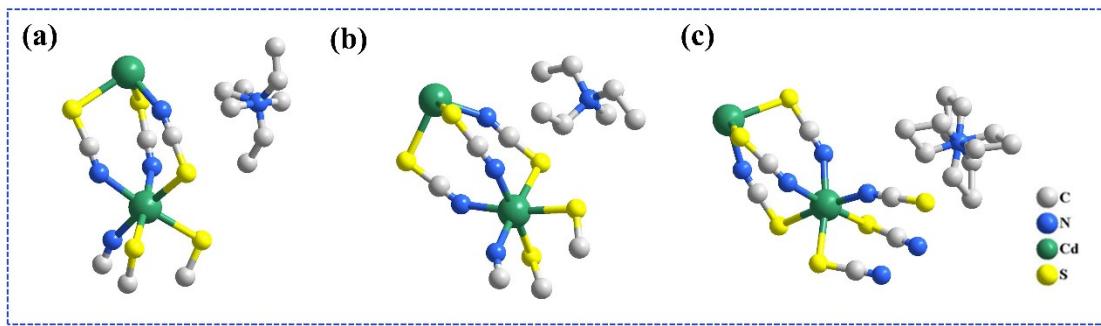
Fig. S6 (a) Molecular structure of [DEDMA][Cd(SCN)$_3$] at 298 K (containing [Cd(SCN)$_3$]$^-$ chains and [DEDMA]$^+$ cations). (b) Molecular structure of [TEMA][Cd(SCN)$_3$] at 286 K (containing [Cd(SCN)$_3$]$^-$ chains and [TEMA]$^+$ cations). (c) Molecular structure of [TEA][Cd(SCN)$_3$] at 293 K (containing [Cd(SCN)$_3$]$^-$ chains and [TEA]$^+$ cations).

Structure occupies (A^3) 565.23 (37.93%)

Structure occupies (A^3) 564.41 (36.23%)

Structure occupies (A^3) 565.54 (34.43%)

Structure occupies (A^3) 563.22 (31.76%)
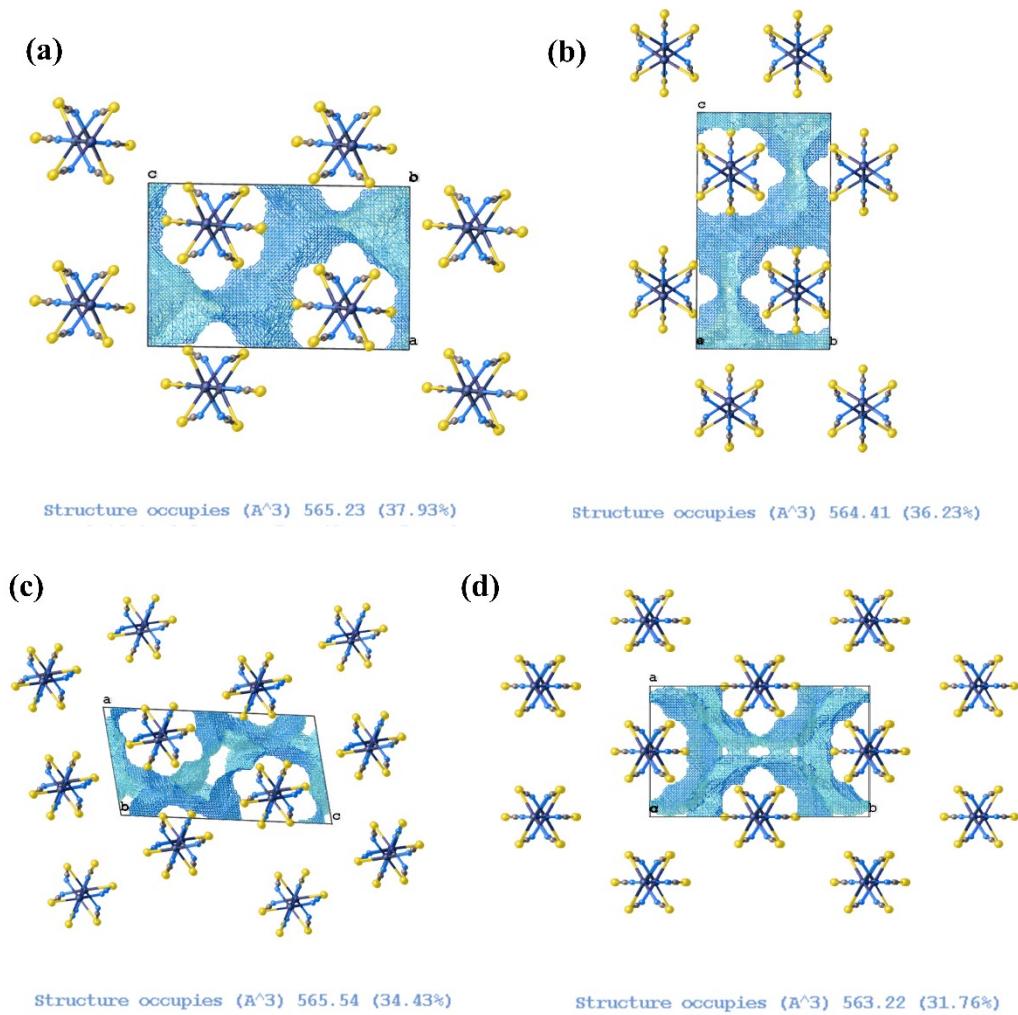
Fig. S7 (a) Void diagram between anionic frameworks in unit cell of [TMEA][Cd(SCN)$_3$]. (b) Void diagram between anionic frameworks in unit cell of [DEDMA][Cd(SCN)$_3$]. (c) Void diagram between anionic frameworks in unit cell of [TEMA][Cd(SCN)$_3$]. (d) Void diagram between anionic frameworks in unit cell of [TEA][Cd(SCN)$_3$].
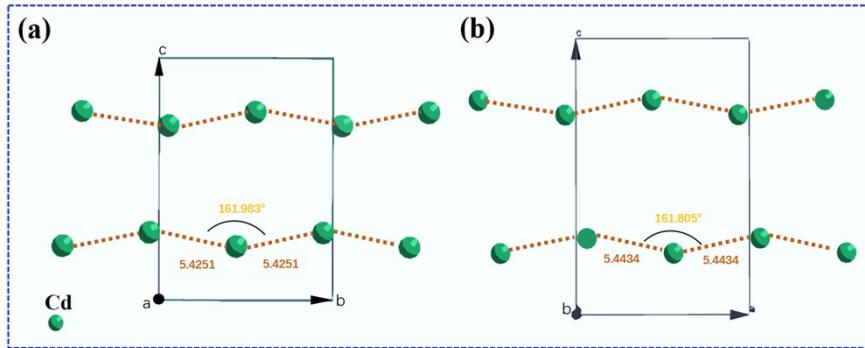
Fig. S8 Cd-Cd-Cd anion chains arrangement in compounds [TMEA][Cd(SCN)$_3$] (a) and [DEDMA][Cd(SCN)$_3$] (b).
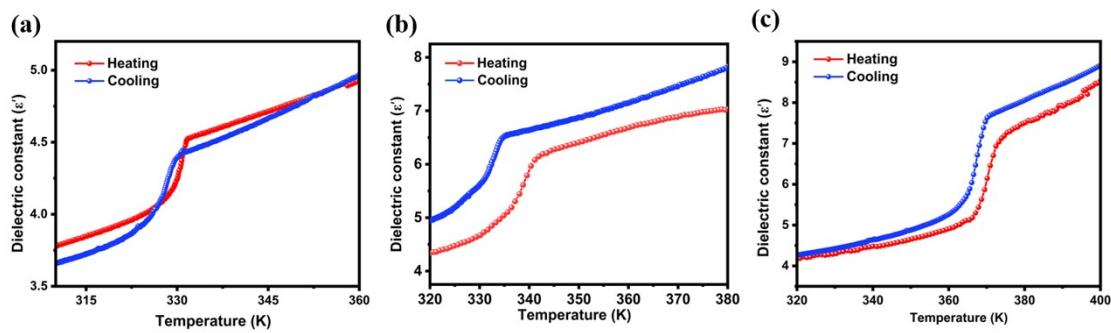
Fig. S9 Temperature-dependent dielectric constant (ε') in a heating-cooling cycle of (a) [DEDMA][Cd(SCN)$_3$], (b) [TEMA][Cd(SCN)$_3$], and (c) [TEA][Cd(SCN)$_3$].
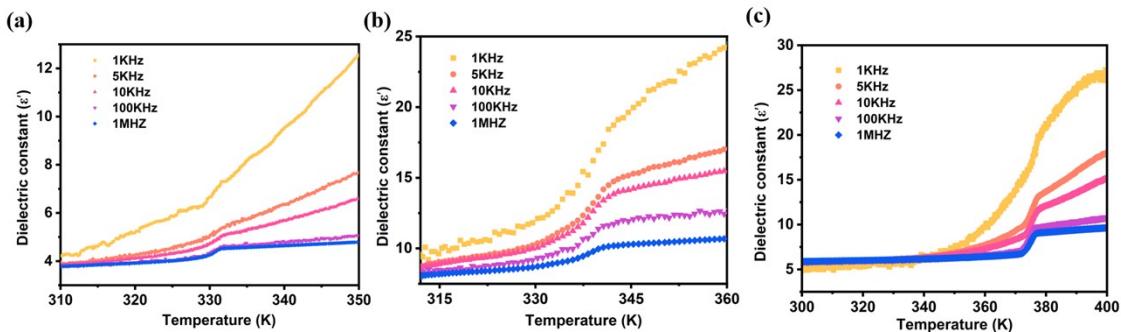
Fig. S10 Temperature dependence of the real part (ε') of (a) [DEDMA][Cd(SCN)$_3$], (b) [TEMA][Cd(SCN)$_3$] and (c) [TEA][Cd(SCN)$_3$] during the heating process at different frequencies.
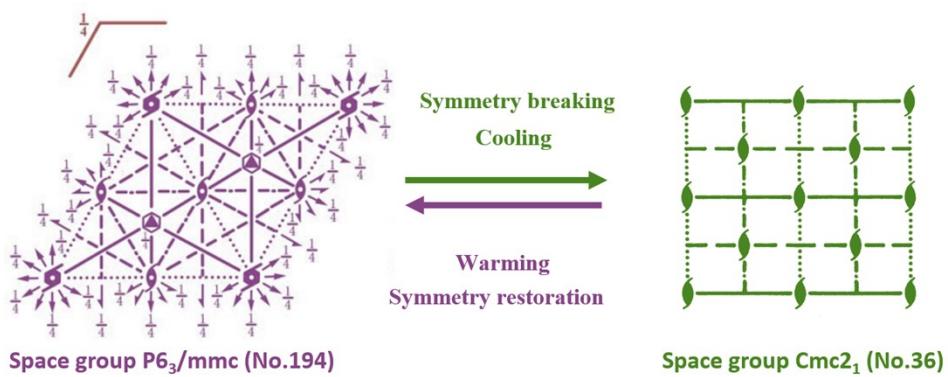
Fig. S11 Symmetry transformations of space group from $P6_3/mmc$ to $Cmc2_1$ for [TEA][Cd(SCN)$_3$].
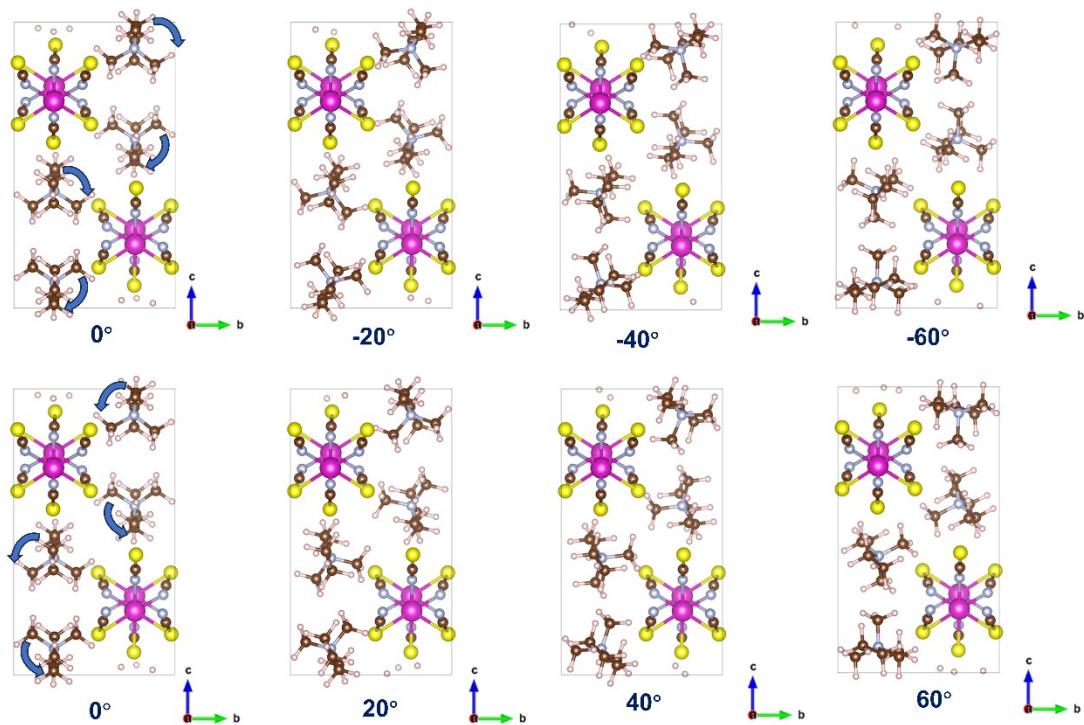
Fig. S12 The Computational models of the energy barrier for the rotation of [DEDMA][Cd(SCN)$_3$].
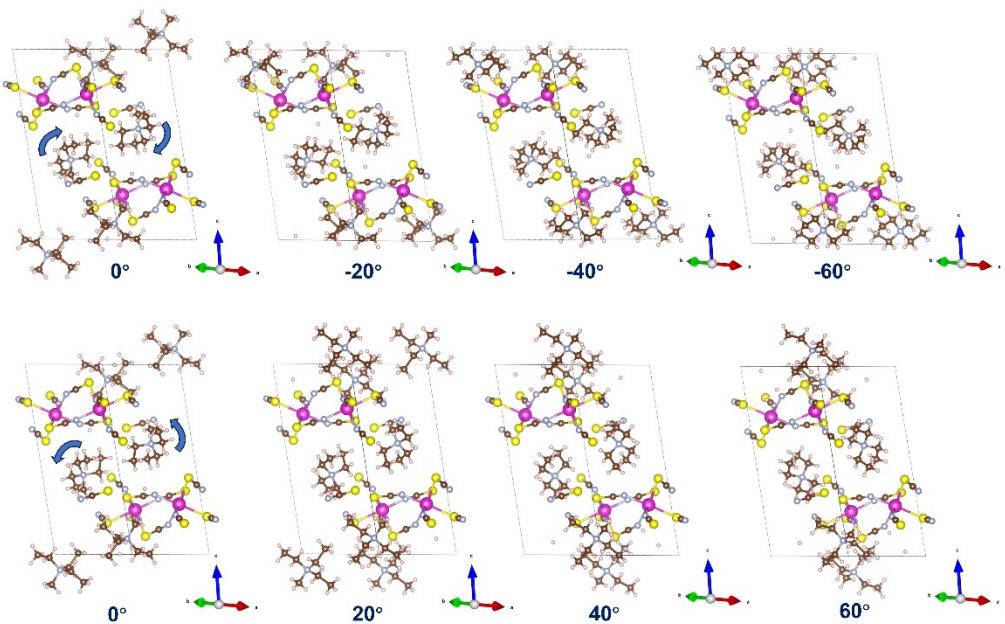
Fig. S13 The Computational models of the energy barrier for the rotation of [TEMA][Cd(SCN)$_3$].
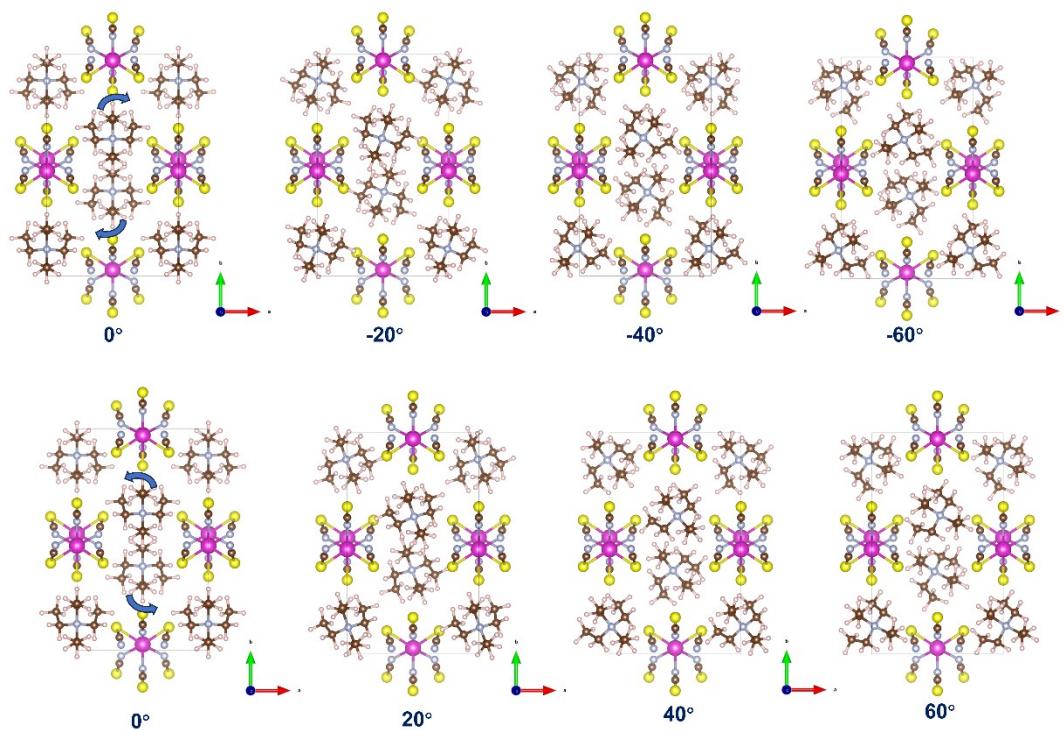
Fig. S14 The Computational models of the energy barrier for the rotation of [TEA][Cd(SCN)$_3$].

Table S1 Crystal data and structure refinement for [TMEA][Cd(SCN)$_3$] at 293 K.

Compound	[TMEA][Cd(SCN)$_3$]
Temperature	293 K
Empirical formula	C$_8$H$_{14}$CdN$_4$S$_3$
Formula weight	374.837
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.3109(7)
b/Å	10.7164(6)
c/Å	14.9364(11)
α/°	90
β/°	90.634(7)
γ/°	90
V/Å^3	1490.25(18)
Z	4
F(000)	742.4
Radiation	Mo Kα (λ = 0.71073)
GOF	1.065
R_1[I>=2σ (I)]	0.0784
wR$_2$[I>=2σ (I)]	0.2333

Table S2 Crystal data and structure refinement for [DEDMA][Cd(SCN)$_3$] at 298 K and 343K.

Compound	[DEDMA][Cd(SCN)$_3$]	
Temperature	298.45(10) K	343.0 K
Empirical formula	C$_9$H$_{16}$CdN$_4$S$_3$	C$_9$CdN$_4$S$_3$
Formula weight	388.84	372.71
Crystal system	orthorhombic	hexagonal
Space group	$Pnma$	$P6_3/mmc$
a/Å	10.7498(7)	9.448(2)
b/Å	9.0463(8)	9.448(2)
c/Å	16.0214(13)	10.894(2)
α/°	90	90.00(3)
β/°	90	90.00(3)
γ/°	90	120.00(3)
V/Å^3	1558.0(2)	842.1(4)
Z	4	2
F(000)	776.0	356.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
GOF	1.072	1.023
R_1[I>=2σ (I)]	0.0854	0.1070
wR$_2$[I>=2σ (I)]	0.2717	0.2122

Table S3 Crystal data and structure refinement for [TEMA][Cd(SCN)$_3$] at 286 K and 353 K.

Compound	[TEMA][Cd(SCN)$_3$]	
Temperature	286.00 K	353.00 K
Empirical formula	C$_{10}$H$_{18}$CdN$_4$S$_3$	C$_{10}$CdN$_4$S$_3$
Formula weight	402.86	384.72
Crystal system	monoclinic	hexagonal
Space group	$P2_1/c$	$P6_3/mmc$
a/Å	8.984(2)	9.703(2)
b/Å	10.779(2)	9.703(2)
c/Å	17.325(5)	10.837(2)
α/°	90	90.00(3)
β/°	101.771(7)	90.00(3)
γ/°	90	120.00(3)
V/Å^3	1642.4(7)	883.5(4)
Z	4	2
F(000)	808.0	368.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
GOF	1.028	1.086
R$_1$[I>=2σ (I)]	0.0716	0.1329
wR$_2$[I>=2σ (I)]	0.2233	0.2879

Table S4 Crystal data and structure refinement for [TEA][Cd(SCN)$_3$] at 293 K and 393 K.

Compound	[TEA][Cd(SCN)$_3$]	
Temperature	293(2) K	393.01(10) K
Empirical formula	C$_{11}$CdN$_4$S$_3$	C$_{11}$CdN$_4$S$_3$
Formula weight	396.73	396.73
Crystal system	orthorhombic	hexagonal
Space group	$Cmc2_1$	$P6_3/mmc$
a/Å	9.8887(5)	9.989(2)
b/Å	16.6064(6)	9.989(2)
c/Å	10.7989(4)	10.798(2)
α/°	90	90
β/°	90	90
γ/°	90	120
V/Å^3	1773.35(13)	933.1(4)
Z	2	2
F(000)	760.0	380.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
GOF	1.094	1.193
R$_1$[I>=2σ (I)]	0.0314	0.1401
wR$_2$[I>=2σ (I)]	0.0866	0.2672

Table S5 The Void volume and Void occupancy of four compounds. Delete cations in each crystal cell and calculate the remaining void volume through OLEX2 software (Resolution 0.2 Å).

	[TMEA][Cd(SCN)₃]	[DEDMA][Cd(SCN)₃]	[TEMA][Cd(SCN)₃]	[TEA][Cd(SCN)₃]
Cell volume(Å³)	1490.25(18)	1558.0(2)	1640.8(3)	1773.35(13)
void volume(Å³)	565.66	564.3	565.13	563.17
Void occupancy	37.96%	36.22%	34.44%	31.76%

Table S6 The energy barrier for the different rotation angles of compounds [DEDMA][Cd(SCN)₃], [TEMA][Cd(SCN)₃], and [TEA][Cd(SCN)₃].

Rotation angle (Degree)	Energy for [DEDMA][Cd(SCN)₃] (eV)	Energy for [TEMA][Cd(SCN)₃] (eV)	Energy for [TEA][Cd(SCN)₃] (eV)
-60	1.72	7.05	9.71
-40	0.96	3.09	6.24
-20	-0.04	0.41	2.3
0	0	0	0
20	-0.07	0.53	2.3
40	0.66	2.4	6.09
60	1.43	5.1	9.7

Table S7 Datas related to cadmium thiocyanate one-dimensional hybrid materials.

Compound	Void occupancy	Cd-Cd distances (Å)	T_p (K)	Ref
[CPtmp][Cd(SCN)₃]	31.37%	9.209	247/335/349 K	[4]
[(CH₃)₃PCH₂F][Cd(SCN)₃]	38.66%	7.511	318 K	[5]
[(CH₃)₄P][Cd(SCN)₃]	38.51%	7.636	308 K	[5]
[(CH₃)₃PCH₂OH][Cd(SCN)₃]	38.66%	7.641	248.5 K	[6]
[R-(HASD)][Cd(SCN)₃]	32.96%	8.873	365 K	[7]
[S-(HASD)][Cd(SCN)₃]	32.95%	8.881	365 K	[7]
[(i-PrNHMe₂)][Cd(SCN)₃]	38.38%	8.708	328 K	[8]
[(MeNHEt₂)][Cd(SCN)₃]	39.48%	8.849	345 K	[8]
[FMPD][Cd(SCN)₃]	34.58%	7.995	302.5/352.5 K	[9]
[DMIE][Cd(SCN)₃]	41.67%	9.360	248.6 K	[10]
[DMIFE][Cd(SCN)₃]	34.25%	9.156	295.9 K	[10]
[DMICE][Cd(SCN)₃]	33.05%	9.262	335.1 K	[10]
[DMIBE][Cd(SCN)₃]	32.75%	9.333	367.8 K	[10]
[C₂H₁₀N₂]Cd(SCN)₄]	53.87%	7.908	/	[11]
[(CH₃)₄N][Cd(SCN)₃]	41.14%	7.616	/	[12]
[(CH₃)₄N]₂[Cd(SCN)₄]]	34.35%	7.300	/	[12]
[H₂(tmen)][Cd(SCN)₄]	40.70%	8.131	/	[13]
[H₂(tmba)][Cd₂(SCN)₆]	44.14%	7.444	/	[13]

[H$_2$(L$_2$)][Cd(SCN)$_4$]	32.83%	9.361	/	14
[(C$_3$H$_7$)$_4$N][Cd(SCN)$_3$]	25.54%	9.371	/	15
[TMEA][Cd(SCN)$_3$]	37.96%	8.181	/	This work
[DEDMA][Cd(SCN)$_3$]	36.22%	8.565	333 K	This work
[TEMA][Cd(SCN)$_3$]	34.44%	8.416	342 K	This work
[TEA][Cd(SCN)$_3$]	31.76%	9.664	375 K	This work

Table S8 The bond lengths (Å) and angles (°) of [TMEA][Cd(SCN)$_3$] in the RTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Cd1–S1[1]	2.737(2)	S1–Cd1–S2	85.67(9)
Cd1–S2[2]	2.740(3)	S1–Cd1–S3	85.53(9)
Cd1–S3[2]	2.751(3)	S2–Cd1–S3	97.32(10)
Cd1–N2	2.309(8)	N2–Cd1–S1	176.89(19)
Cd1–N3	2.364(8)	N2–Cd1–S2	92.4(2)
Cd1–N4	2.389(10)	N2–Cd1–S3	92.3(2)
S1–C6	1.644(8)	N2–Cd1–N3	91.0(3)
S2–C7	1.600(9)	N2–Cd1–N4	90.2(3)
S3–C8	1.594(9)	N3–Cd1–S1	91.2(2)
N2–C6	1.143(10)	N3–Cd1–S2	172.6(2)
N3–C7	1.176(10)	N3–Cd1–S3	89.1(2)
N4–C8	1.190(11)	N3–Cd1–N4	85.3(3)
N1–C5	1.473(9)	N4–Cd1–S1	92.2(2)
N1–C4	1.468(9)	N4–Cd1–S2	88.2(2)
N1–C2	1.463(9)	N4–Cd1–S3	173.9(3)
N1–C3	1.483(7)	C6–S1–Cd1	95.9(3)
C5–H5A	0.9600	C7–S2–Cd1	98.2(3)
C5–H5B	0.9600	C8–S3–Cd1	98.8(3)
C5–H5C	0.9600	C6–N2–Cd1	153.6(7)
C4–H4A	0.9600	N2–C6–S1	179.5(8)
C4–H4B	0.9600	C7–N3–Cd1	143.0(8)
C4–H4C	0.9600	N3–C7–S2	175.1(9)
C2–H2A	0.9700	C8–N4–Cd1	139.3(9)
C2–H2B	0.9700	C5–N1–C3	112.5(19)
C2–C1	1.5400(10)	C4–N1–C5	104.7(19)
C1–H1A	0.9601	C4–N1–C3	106.5(17)
C1–H1B	0.9603	C2–N1–C5	115.3(19)
C1–H1C	0.9600	C2–N1–C4	117.6(19)
C3–H3A	0.9599	C2–N1–C3	100.1(16)
C3–H3B	0.9598	N4–C8–S3	173.2(9)
C3–H3C	0.9601	N1–C5–H5A	109.5
		N1–C5–H5B	109.5
		N1–C5–H5C	109.5
		H5A–C5–H5B	109.5

H5A–C5–H5C	109.5	
H5B–C5–H5C	109.5	
N1–C4–H4A	109.5	
N1–C4–H4B	109.5	
N1–C4–H4C	109.5	
H4A–C4–H4B	109.5	
H4A–C4–H4C	109.5	
H4B–C4–H4C	109.5	
N1–C2–H2A	112.1	
N1–C2–H2B	112.1	
N1–C2–C1	98.4(17)	
H2A–C2–H2B	109.7	
C1–C2–H2A	112.1	
C1–C2–H2B	112.1	
C2–C1–H1A	117.7	
C2–C1–H1B	107.4	
C2–C1–H1C	103.0	
H1A–C1–H1B	109.5	
H1A–C1–H1C	109.5	
H1B–C1–H1C	109.5	
N1–C3–H3A	114.9	
N1–C3–H3B	109.9	
N1–C3–H3C	103.4	
H3A–C3–H3B	109.5	
H3A–C3–H3C	109.5	
H3B–C3–H3C	109.5	

Symmetry codes: [1] −x+1/2, y−1/2, −z+3/2; [2] −x+1/2, y+1/2, −z+3/2.

Table S9 The bond lengths (Å) and angles (º) of [DEDMA][Cd(SCN)$_3$] in the RTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
C1–H1A	0.9600	H1A–C1–H1B	109.5
C1–H1B	0.9600	H1A–C1–H1C	109.5
C1–H1C	0.9600	H1B–C1–H1C	109.5
C1–N1	1.510(6)	N1–C1–H1A	109.5
C2–H2A	0.9600	N1–C1–H1B	109.5
C2–H2B	0.9600	N1–C1–H1C	109.5
C2–H2C	0.9600	H2A–C2–H2B	109.5
C2–C3	1.313(16)	H2A–C2–H2C	109.5
C3–H3A	0.9700	H2B–C2–H2C	109.5
C3–H3B	0.9700	C3–C2–H2A	109.5
C3–N1	1.425(12)	C3–C2–H2B	109.5
C4–H4A	0.9600	C3–C2–H2C	109.5
C4–H4B	0.9601	C2–C3–H3A	105.2

C4–H4C	0.9598	C2–C3–H3B	105.2
C4–C5	1.420(18)	C2–C3–N1	128.5(12)
C5–H5A	0.9700	H3A–C3–H3B	105.9
C5–H5B	0.9700	N1–C3–H3A	105.2
C5–N1	1.362(13)	N1–C3–H3B	105.2
N1–C1A[1]	1.491(13)	H4A–C4–H4B	109.5
N1–C1A	1.491(13)	H4A–C4–H4C	109.5
C6–N2	1.131(7)	H4B–C4–H4C	109.5
C6–S1	1.632(5)	C5–C4–H4A	109.6
C7–N3	1.174(11)	C5–C4–H4B	109.4
C7–S2	1.603(8)	C5–C4–H4C	109.4
Cd1–N2	2.376(7)	C4–C5–H5A	103.9
Cd1–N2[2]	2.376(7)	C4–C5–H5B	103.9
Cd1–N3	2.271(8)	H5A–C5–H5B	105.4
Cd1–S1[3]	2.756(2)	N1–C5–C4	133.5(14)
Cd1–S1[4]	2.756(2)	N1–C5–H5A	103.9
Cd1–S2[5]	2.704(3)	N1–C5–H5B	103.9
C1A–H1AA	0.9600	C1–N1–C1	167.6(11)
C1A–H1AB	0.9600	C3–N1–C1	96.2(5)
C1A–H1AC	0.9600	C3–N1–C1	96.2(5)
		C3–N1–C1A	115.0(10)
		C3–N1–C1A	115.0(10)
		C5–N1–C1	86.8(6)
		C5–N1–C1	86.8(6)
		C5–N1–C3	124.0(10)
		C5–N1–C1A	116.8(11)
		C5–N1–C1A	116.8(11)
		N2–C6–S1	175.9(7)
		N3–C7–S2	178.6(8)
		N2–Cd1–N2	83.4(4)
		N2–Cd1–S1	90.92(19)
		N2–Cd1–S1	173.58(17)
		N2–Cd1–S1	90.92(18)
		N2–Cd1–S1	173.58(17)
		N2–Cd1–S2	91.59(13)
		N2–Cd1–S2	91.59(13)
		N3–Cd1–N2	92.1(2)
		N3–Cd1–N2	92.1(2)
		N3–Cd1–S1	91.13(14)
		N3–Cd1–S1	91.13(14)
		N3–Cd1–S2	175.1(2)
		S1–Cd1–S1	94.58(9)
		S2–Cd1–S1	85.55(5)
		S2–Cd1–S1	85.55(5)

C6–N2–Cd1	143.0(7)
C7–N3–Cd1	158.5(7)
C6–S1–Cd1	99.1(2)
C7–S2–Cd1	95.9(3)
N1–C1A–H1AA	109.5
N1–C1A–H1AB	109.5
N1–C1A–H1AC	109.5
H1AA–C1A–H1AB	109.5
H1AA–C1A–H1AC	109.5
H1AB–C1A–H1AC	109.5

Symmetry codes: [1] x, −y+3/2, z; [2] x, −y+1/2, z; [3] x−1/2, y, −z+3/2; [4] x−1/2, −y+1/2, −z+3/2; [5] x+1/2, y, −z+3/2.

Table S10 The bond lengths (Å) and angles (º) of [TEMA][Cd(SCN)$_3$] in the RTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Cd1–S1[1]	2.736(2)	S1–Cd1–S2	96.21(6)
Cd1–S2[1]	2.741(2)	S1–Cd1–S3	85.66(7)
Cd1–S3[2]	2.766(2)	S2–Cd1–S3	84.02(7)
Cd1–N2	2.342(6)	N2–Cd1–S1	171.98(17)
Cd1–N3	2.275(6)	N2–Cd1–S2	90.56(18)
Cd1–N4	2.340(6)	N2–Cd1–S3	90.80(19)
S1–C8	1.644(7)	N3–Cd1–S1	92.52(17)
S2–C9	1.638(7)	N3–Cd1–S2	92.36(17)
S3–C10	1.654(7)	N3–Cd1–S3	175.75(16)
N2–C8	1.165(9)	N3–Cd1–N2	91.5(2)
N3–C10	1.159(9)	N3–Cd1–N4	93.8(2)
N4–C9	1.156(8)	N4–Cd1–S1	89.71(17)
N1–C2	1.505(11)	N4–Cd1–S2	171.22(17)
N1–C5	1.502(9)	N4–Cd1–S3	89.99(17)
N1–C6	1.504(10)	N4–Cd1–N2	83.1(3)
N1–C11	1.560(11)	C8–S1–Cd1	98.0(2)
C2–H2A	0.9700	C9–S2–Cd1	100.1(2)
C2–H2B	0.9700	C10–S3–Cd1	95.4(2)
C2–C3	1.493(17)	C8–N2–Cd1	148.2(6)
C3–H3A	0.9600	C10–N3–Cd1	154.9(6)
C3–H3B	0.9600	C9–N4–Cd1	143.5(6)
C3–H3C	0.9600	N2–C8–S1	178.8(7)
C4–H4A	0.9600	N4–C9–S2	178.1(7)
C4–H4B	0.9600	N3–C10–S3	179.4(7)
C4–H4C	0.9600	C2–N1–C11	106.4(7)
C4–C5	1.532(13)	C5–N1–C2	114.2(7)
C5–H5A	0.9700	C5–N1–C6	107.4(6)
C5–H5B	0.9700	C5–N1–C11	110.9(7)

C6–H6A	0.9600	C6–N1–C2	109.6(7)
C6–H6B	0.9600	C6–N1–C11	108.2(7)
C6–H6C	0.9600	N1–C2–H2A	108.9
C7–H7A	0.9600	N1–C2–H2B	108.9
C7–H7B	0.9600	H2A–C2–H2B	107.7
C7–H7C	0.9600	C3–C2–N1	113.5(10)
C7–C11	1.480(15)	C3–C2–H2A	108.9
C11–H11A	0.9700	C3–C2–H2B	108.9
C11–H11B	0.9700	C2–C3–H3A	109.5
		C2–C3–H3B	109.5
		C2–C3–H3C	109.5
		H3A–C3–H3B	109.5
		H3A–C3–H3C	109.5
		H3B–C3–H3C	109.5
		H4A–C4–H4B	109.5
		H4A–C4–H4C	109.5
		H4B–C4–H4C	109.5
		C5–C4–H4A	109.5
		C5–C4–H4B	109.5
		C5–C4–H4C	109.5
		N1–C5–C4	114.4(7)
		N1–C5–H5A	108.7
		N1–C5–H5B	108.7
		C4–C5–H5A	108.7
		C4–C5–H5B	108.7
		H5A–C5–H5B	107.6
		N1–C6–H6A	109.5
		N1–C6–H6B	109.5
		N1–C6–H6C	109.5
		H6A–C6–H6B	109.5
		H6A–C6–H6C	109.5
		H6B–C6–H6C	109.5
		H7A–C7–H7B	109.5
		H7A–C7–H7C	109.5
		H7B–C7–H7C	109.5
		C11–C7–H7A	109.5
		C11–C7–H7B	109.5
		C11–C7–H7C	109.5
		N1–C11–H11A	108.1
		N1–C11–H11B	108.1
		C7–C11–N1	116.7(8)
		C7–C11–H11A	108.1
		C7–C11–H11B	108.1
		H11A–C11–H11B	107.3

Table S11 The bond lengths (Å) and angles (º) of [TEA][Cd(SCN)$_3$] in the RTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Cd1–S1[1]	2.7460(17)	S1–Cd1–S1	97.44(8)
Cd1–S1[2]	2.7460(17)	S2–Cd1–S1	85.31(4)
Cd1–S2[3]	2.733(2)	S2–Cd1–S1	85.31(4)
Cd1–N1[4]	2.335(6)	N1–Cd1–S1	170.87(15)
Cd1–N1	2.335(6)	N1–Cd1–S1	90.34(16)
Cd1–N2	2.263(6)	N1–Cd1–S1	90.33(16)
S1–C1	1.630(5)	N1–Cd1–S1	170.87(15)
S2–C2	1.636(7)	N1–Cd1–S2	90.57(14)
N1–C1	1.145(7)	N1–Cd1–S2	90.57(14)
N2–C2	1.158(10)	N1–Cd1–N1	81.5(3)
C3–N3	1.517(10)	N2–Cd1–S1	90.35(11)
C3–C4	1.492(18)	N2–Cd1–S1	90.35(11)
N3–C5	1.486(9)	N2–Cd1–S2	173.42(16)
N3–C5[5]	1.486(9)	N2–Cd1–N1	94.41(18)
N3–C9	1.500(9)	N2–Cd1–N1	94.41(18)
N3–C9[5]	1.500(9)	C1–S1–Cd1	99.70(18)
N3–C7[5]	1.513(9)	C2–S2–Cd1	95.2(2)
N3–C7	1.513(9)	C1–N1–Cd1	148.0(5)
C5–C6	1.570(16)	C2–N2–Cd1	158.3(5)
C8–C9[5]	1.512(16)	N1–C1–S1	179.1(6)
C8–C7	1.539(14)	N2–C2–S2	179.3(6)
		C4–C3–N3	116.9(9)
		C3–N3–C3	62.2(12)
		C5–N3–C3	112.2(9)
		C5–N3–C3	79.1(8)
		C5–N3–C3	79.1(8)
		C5–N3–C3	112.2(9)
		C5–N3–C5	66.6(11)
		C5–N3–C9	172.0(10)
		C5–N3–C9	110.5(8)
		C5–N3–C9	172.0(10)
		C5–N3–C9	110.5(8)
		C5–N3–C7	62.2(7)
		C5–N3–C7	107.8(8)
		C5–N3–C7	107.8(8)
		C5–N3–C7	62.2(7)
		C9–N3–C3	108.8(8)
		C9–N3–C3	108.8(8)
		C9–N3–C3	73.8(8)
		C9–N3–C3	73.8(8)

C9–N3–C9	71.4(11)
C9–N3–C7	64.8(7)
C9–N3–C7	113.3(8)
C9–N3–C7	64.8(7)
C9–N3–C7	113.3(8)
C7–N3–C3	166.4(9)
C7–N3–C3	104.2(8)
C7–N3–C3	166.4(9)
C7–N3–C3	104.2(8)
C7–N3–C7	89.4(12)
N3–C5–C3	51.2(5)
N3–C5–C6	114.3(8)
C6–C5–C3	118.8(10)
C5–C6–C5	62.6(9)
C3–C4–C3	63.4(10)
C9–C8–C7	63.9(6)
N3–C9–C8	115.6(9)
N3–C7–C8	113.3(8)
N3–C7–C9	57.2(5)
C8–C7–C9	57.2(7)

Symmetry codes: [1] −x+2, −y+1, z+1/2; [2] x, −y+1, z+1/2; [3] −x+2, −y+1, z−1/2; [4] −x+2, y, z; [5] −x+1, y, z.

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