Electronic Supplementary Information (ESI) for

Chiral amino acid-templated tin fluorides tailoring nonlinear optical properties, birefringence, and photoluminescence

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Fig. S1 Experimental and calculated powder X-ray diffraction patterns of (*R*)-Sn(II) and (*S*)-Sn(II).

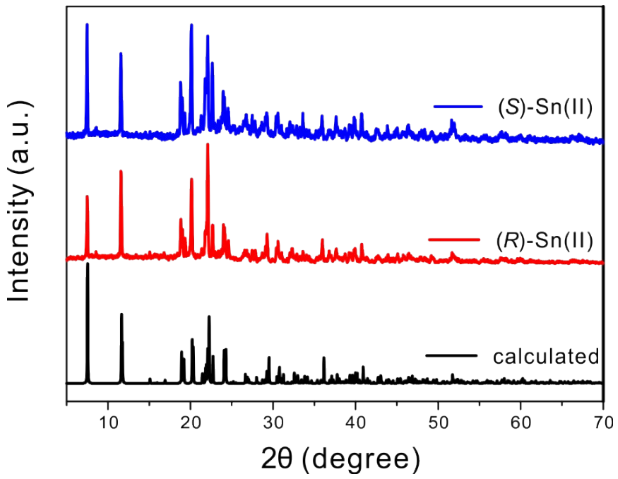

Fig. S2 (a) Experimental and calculated powder X-ray diffraction patterns of (*R*)-Sn(IV) and (*S*)-Sn(IV), and (b) photograph of an as-grown single crystal.

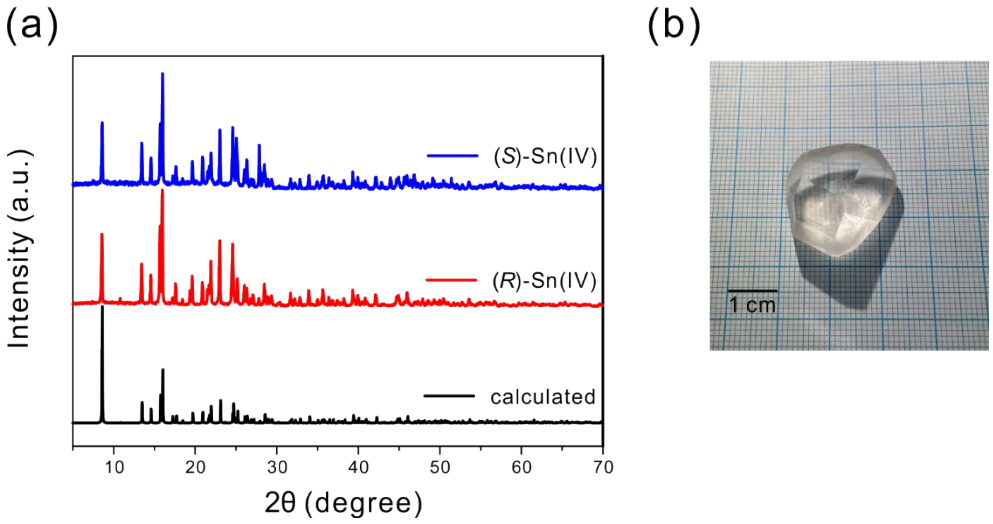

Table S1. Crystallographic data for (*R*)-Sn(II), (*S*)-Sn(II), (*R*)-Sn(IV), and (*S*)-Sn(IV).

	(*R*)-Sn(II)	(*S*)-Sn(II)	(*R*)-Sn(IV)	(*S*)-Sn(IV)
formula	$C_8H_{10}NO_3SnF_3$		$C_{16}H_{20}N_2O_6SnF_6$	
fw	343.86	343.86	569.03	569.03
Space group	$P2_1$	$P2_1$	$P2_12_12$	$P2_12_12$
a (Å)	7.9805(2)	7.9798(3)	13.4115(4)	13.4225(4)
b (Å)	5.8498(2)	5.8516(2)	7.5092(2)	7.5081(2)
c (Å)	23.4594(7)	23.4718(9)	10.2740(3)	10.2706(3)
α (°)	90	90	90	90
β (°)	90.8340(10)	90.8650(10)	90	90
γ (°)	90	90	90	90
V (Å^3)	1095.07(6)	1095.88(7)	1034.69(5)	1035.05(5)
Z	4	4	2	2
T (K)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm^3)	2.086	2.084	1.826	1.826
$R(F_o)^a$	0.0280	0.0321	0.0176	0.0237
$R_w(F_o^2)^b$	0.0659	0.0793	0.0459	0.0587
Flack x	0.113(15)	0.11(3)	0.09(2)	0.11(3)

$^a R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $^b Rw(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (˚) for (*R*)-Sn(II).

Selected bond distances (Å)			
Sn(1)-F(2)	2.029(3)	C(7)-C(8)	1.526(7)
Sn(1)-F(1)	2.078(3)	C(8)-O(4)	1.211(7)
Sn(1)-F(3)	2.107(3)	C(8)-O(6)	1.310(6)
Sn(2)-F(5)	2.023(3)	C(9)-O(2)	1.365(7)
Sn(2)-F(4)	2.075(3)	C(9)-C(10)	1.380(9)
Sn(2)-F(6)	2.099(4)	C(9)-C(14)	1.381(9)
C(1)-O(5)	1.359(7)	C(10)-C(11)	1.388(9)
C(1)-C(6)	1.383(9)	C(11)-C(12)	1.385(8)
C(1)-C(2)	1.385(9)	C(12)-C(13)	1.391(8)
C(2)-C(3)	1.397(8)	C(12)-C(15)	1.523(7)
C(3)-C(4)	1.389(8)	C(13)-C(14)	1.393(8)
C(4)-C(5)	1.393(7)	C(15)-N(2)	1.491(7)
C(4)-C(7)	1.517(7)	C(15)-C(16)	1.518(7)
C(5)-C(6)	1.388(8)	C(16)-O(3)	1.204(7)
C(7)-N(1)	1.491(7)	C(16)-O(1)	1.312(7)
Selected bond angles (˚)			
F(2)-Sn(1)-F(1)	84.20(14)	O(4)-C(8)-O(6)	125.2(5)
F(2)-Sn(1)-F(3)	81.82(13)	O(4)-C(8)-C(7)	122.6(5)
F(1)-Sn(1)-F(3)	87.79(14)	O(6)-C(8)-C(7)	112.1(5)
F(5)-Sn(2)-F(4)	83.95(14)	O(2)-C(9)-C(10)	116.8(6)
F(5)-Sn(2)-F(6)	81.68(14)	O(2)-C(9)-C(14)	122.9(5)

F(4)-Sn(2)-F(6)	88.86(14)	C(10)-C(9)-C(14)	120.3(5)
O(5)-C(1)-C(6)	117.8(6)	C(9)-C(10)-C(11)	119.4(6)
O(5)-C(1)-C(2)	122.0(6)	C(12)-C(11)-C(10)	121.2(6)
C(6)-C(1)-C(2)	120.2(5)	C(11)-C(12)-C(13)	119.0(5)
C(1)-C(2)-C(3)	119.5(6)	C(11)-C(12)-C(15)	119.3(5)
C(4)-C(3)-C(2)	120.4(5)	C(13)-C(12)-C(15)	121.5(5)
C(3)-C(4)-C(5)	119.5(5)	C(12)-C(13)-C(14)	120.0(6)
C(3)-C(4)-C(7)	122.0(5)	C(9)-C(14)-C(13)	120.1(6)
C(5)-C(4)-C(7)	118.5(5)	N(2)-C(15)-C(16)	107.8(5)
C(6)-C(5)-C(4)	119.9(6)	N(2)-C(15)-C(12)	109.8(4)
C(1)-C(6)-C(5)	120.4(6)	C(16)-C(15)-C(12)	113.1(4)
N(1)-C(7)-C(4)	110.9(4)	O(3)-C(16)-O(1)	125.8(5)
N(1)-C(7)-C(8)	107.4(4)	O(3)-C(16)-C(15)	122.1(5)
C(4)-C(7)-C(8)	111.3(5)	O(1)-C(16)-C(15)	112.1(5)

Table S3. Hydrogen bond distances (Å) for (*R*)-Sn(II).

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1A)...F(1)#1	2.702(6)	N(2)-H(2C)...F(5)#4	2.699(7)
N(1)-H(1B)...O(4)#1	2.875(6)	O(1)-H(1O)...F(6)	2.585(5)
N(1)-H(1B)...F(3)#1	3.027(6)	O(2)-H(2O)...F(1)#5	2.633(6)
N(1)-H(1C)...F(2)#2	2.697(6)	O(5)-H(5O)...F(4)	2.586(6)
N(2)-H(2A)...F(4)#3	2.728(6)	O(6)-H(6O)...F(3)	2.565(5)
N(2)-H(2B)...O(3)#3	2.866(6)		
Symmetry operation: #1 -x,y+1/2,-z+2 #2 -x,y-1/2,-z+2 #3 -x+1,y-1/2,-z+1 #4 -x+1,y+1/2,-z+1 #5 x,y,z-1			

Table S4. Selected bond distances (Å) and bond angles (˚) for (*S*)-Sn(II).

Selected bond distances (Å)			
F(2)-Sn(1)	2.028(4)	C(7)-C(8)	1.537(8)
F(3)-Sn(1)	2.113(4)	C(8)-O(4)	1.206(8)
F(4)-Sn(2)	2.073(4)	C(8)-O(6)	1.311(7)
F(5)-Sn(2)	2.028(4)	C(9)-O(2)	1.369(7)
F(6)-Sn(2)	2.100(4)	C(9)-C(14)	1.383(9)
Sn(1)-F(1)	2.085(4)	C(9)-C(10)	1.396(10)
C(2)-C(1)	1.386(10)	C(10)-C(11)	1.388(9)
C(2)-C(3)	1.393(9)	C(11)-C(12)	1.389(8)
C(1)-O(5)	1.358(7)	C(12)-C(13)	1.388(8)
C(1)-C(6)	1.388(9)	C(12)-C(15)	1.519(8)
C(3)-C(4)	1.389(8)	C(13)-C(14)	1.389(8)
C(4)-C(5)	1.384(8)	C(15)-N(2)	1.497(7)
C(4)-C(7)	1.523(7)	C(15)-C(16)	1.498(8)
C(5)-C(6)	1.405(8)	C(16)-O(3)	1.227(8)
C(7)-N(1)	1.483(8)	C(16)-O(1)	1.306(7)
Selected bond angles (˚)			
F(2)-Sn(1)-F(1)	84.27(15)	O(4)-C(8)-O(6)	126.0(5)
F(2)-Sn(1)-F(3)	81.71(14)	O(4)-C(8)-C(7)	122.0(5)
F(1)-Sn(1)-F(3)	87.63(14)	O(6)-C(8)-C(7)	112.0(5)
F(5)-Sn(2)-F(4)	83.83(15)	O(2)-C(9)-C(14)	123.2(6)
F(5)-Sn(2)-F(6)	81.77(15)	O(2)-C(9)-C(10)	116.5(6)

F(4)-Sn(2)-F(6)	88.89(16)	C(14)-C(9)-C(10)	120.3(6)
C(1)-C(2)-C(3)	120.1(6)	C(11)-C(10)-C(9)	119.3(6)
O(5)-C(1)-C(2)	117.5(6)	C(10)-C(11)-C(12)	120.8(6)
O(5)-C(1)-C(6)	122.4(6)	C(13)-C(12)-C(11)	119.2(5)
C(2)-C(1)-C(6)	120.1(5)	C(13)-C(12)-C(15)	121.6(6)
C(4)-C(3)-C(2)	120.3(6)	C(11)-C(12)-C(15)	118.9(6)
C(5)-C(4)-C(3)	119.4(5)	C(12)-C(13)-C(14)	120.5(6)
C(5)-C(4)-C(7)	121.8(5)	C(9)-C(14)-C(13)	119.9(6)
C(3)-C(4)-C(7)	118.8(5)	N(2)-C(15)-C(16)	108.4(5)
C(4)-C(5)-C(6)	120.6(6)	N(2)-C(15)-C(12)	110.2(5)
C(1)-C(6)-C(5)	119.4(6)	C(16)-C(15)-C(12)	113.4(5)
N(1)-C(7)-C(4)	110.9(5)	O(3)-C(16)-O(1)	124.7(5)
N(1)-C(7)-C(8)	107.8(5)	O(3)-C(16)-C(15)	122.0(5)
C(4)-C(7)-C(8)	111.3(5)	O(1)-C(16)-C(15)	113.3(5)

Table S5. Hydrogen bond distances (Å) for (*S*)-Sn(II).

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1A)...F(1)#1	2.699(6)	N(2)-H(2C)...O(3)#3	2.861(6)
N(1)-H(1C)...F(2)#2	2.706(7)	O(1)-H(1O)...F(5)	3.085(6)
N(1)-H(1B)...F(3)#1	3.021(6)	O(1)-H(1O)...F(6)	2.595(6)
N(1)-H(1B)...O(4)#1	2.877(7)	O(2)-H(2O)...F(1)#5	2.630(6)
N(2)-H(2A)...F(4)#3	2.724(6)	O(5)-H(5O)...F(4)	2.589(6)
N(2)-H(2B)...F(5)#4	2.702(7)	O(6)-H(6O)...F(3)	2.570(6)

Symmetry operation: #1 -x+2,y-1/2,-z #2 -x+2,y+1/2,-z #3 -x+1,y+1/2,-z+1
#4 -x+1,y-1/2,-z+1 #5 x,y,z+1

Table S6. Selected bond distances (Å) and bond angles (˚) for (*R*)-Sn(IV).

Selected bond distances (Å)			
Sn(1)-F(2)#1	1.9448(14)	N(1)-C(7)	1.493(3)
Sn(1)-F(2)	1.9448(14)	C(1)-C(6)	1.389(4)
Sn(1)-F(1)#1	1.9608(14)	C(1)-C(2)	1.389(3)
Sn(1)-F(1)	1.9608(14)	C(2)-C(3)	1.388(3)
Sn(1)-F(3)#1	1.9680(15)	C(3)-C(4)	1.399(3)
Sn(1)-F(3)	1.9680(15)	C(4)-C(5)	1.392(3)
O(1)-C(1)	1.371(3)	C(4)-C(7)	1.513(3)
O(2)-C(8)	1.206(3)	C(5)-C(6)	1.397(3)
O(3)-C(8)	1.315(3)	C(7)-C(8)	1.530(4)
Selected bond angles (˚)			
F(2)#1-Sn(1)-F(2)	92.83(9)	O(1)-C(1)-C(2)	116.2(2)
F(2)#1-Sn(1)-F(1)#1	88.67(7)	C(6)-C(1)-C(2)	120.5(2)
F(2)-Sn(1)-F(1)#1	91.82(7)	C(3)-C(2)-C(1)	120.2(2)
F(2)#1-Sn(1)-F(1)	91.82(7)	C(2)-C(3)-C(4)	120.0(2)
F(2)-Sn(1)-F(1)	88.67(7)	C(5)-C(4)-C(3)	119.4(2)
F(1)#1-Sn(1)-F(1)	179.29(9)	C(5)-C(4)-C(7)	119.8(2)
F(2)#1-Sn(1)-F(3)#1	174.53(7)	C(3)-C(4)-C(7)	120.8(2)
F(2)-Sn(1)-F(3)#1	90.89(7)	C(4)-C(5)-C(6)	120.8(2)
F(1)#1-Sn(1)-F(3)#1	87.20(6)	C(1)-C(6)-C(5)	119.2(2)
F(1)-Sn(1)-F(3)#1	92.28(6)	N(1)-C(7)-C(4)	112.8(2)
F(2)#1-Sn(1)-F(3)	90.89(7)	N(1)-C(7)-C(8)	105.52(19)

F(2)-Sn(1)-F(3)	174.53(7)	C(4)-C(7)-C(8)	114.0(2)
F(1)#1-Sn(1)-F(3)	92.28(6)	O(2)-C(8)-O(3)	125.2(3)
F(1)-Sn(1)-F(3)	87.20(6)	O(2)-C(8)-C(7)	121.7(2)
F(3)#1-Sn(1)-F(3)	85.69(10)	O(3)-C(8)-C(7)	113.03(19)
O(1)-C(1)-C(6)	123.3(2)		

Symmetry operation: #1 -x+1,-y,z

Table S7. Hydrogen bond distances (Å) for (*R*)-Sn(IV)

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1N)...F(1)#2	2.972(3)	N(1)-H(3N)...O(1)#5	2.887(3)
N(1)-H(1N)...O(2)#3	2.752(3)	O(1)-H(1O)...F(1)#6	2.699(2)
N(1)-H(2N)...F(2)#4	2.825(3)	O(3)-H(3O)...F(3)	2.559(2)

Symmetry operation: #1 -x+1,-y,z #2 x,y+1,z #3 -x+1/2,y+1/2,-z+2
#4 x-1/2,-y+1/2,-z+2 #5 -x+1/2,y+1/2,-z+1 #6 x,y+1,z-1

Table S8. Selected bond distances (Å) and bond angles (˚) for (*S*)-Sn(IV).

Selected bond distances (Å)			
C(1)-O(1)	1.371(4)	F(3)-Sn(1)	1.965(2)
C(1)-C(6)	1.383(5)	C(2)-C(3)	1.389(5)
C(1)-C(2)	1.387(5)	C(3)-C(4)	1.392(5)
N(1)-C(7)	1.496(4)	C(4)-C(5)	1.395(5)
O(2)-C(8)	1.205(4)	C(4)-C(7)	1.508(5)
O(3)-C(8)	1.312(5)	C(5)-C(6)	1.395(5)
F(1)-Sn(1)	1.958(2)	C(7)-C(8)	1.527(6)
F(2)-Sn(1)	1.941(2)		
Selected bond angles (˚)			
O(1)-C(1)-C(6)	123.2(3)	F(1)-Sn(1)-F(3)	92.12(9)
O(1)-C(1)-C(2)	115.9(3)	F(3)#1-Sn(1)-F(3)	85.65(14)
C(6)-C(1)-C(2)	120.9(3)	C(1)-C(2)-C(3)	119.9(3)
F(2)-Sn(1)-F(2)#1	92.91(14)	C(2)-C(3)-C(4)	120.3(3)
F(2)-Sn(1)-F(1)#1	88.80(10)	C(3)-C(4)-C(5)	119.0(3)
F(2)#1-Sn(1)-F(1)#1	91.77(10)	C(3)-C(4)-C(7)	121.1(3)
F(2)-Sn(1)-F(1)	91.76(10)	C(5)-C(4)-C(7)	119.9(3)
F(2)#1-Sn(1)-F(1)	88.80(10)	C(4)-C(5)-C(6)	121.0(3)
F(1)#1-Sn(1)-F(1)	179.17(13)	C(1)-C(6)-C(5)	118.9(3)
F(2)-Sn(1)-F(3)#1	90.85(10)	N(1)-C(7)-C(4)	112.9(3)
F(2)#1-Sn(1)-F(3)#1	174.65(11)	N(1)-C(7)-C(8)	105.7(3)
F(1)#1-Sn(1)-F(3)#1	92.11(10)	C(4)-C(7)-C(8)	114.1(3)

F(1)-Sn(1)-F(3)#1	87.28(9)	O(2)-C(8)-O(3)	125.4(4)
F(2)-Sn(1)-F(3)	174.65(11)	O(2)-C(8)-C(7)	121.6(4)
F(2)#1-Sn(1)-F(3)	90.85(10)	O(3)-C(8)-C(7)	113.0(3)
F(1)#1-Sn(1)-F(3)	87.28(9)		

Symmetry operation: #1 -x+1,-y+2,z

Table S9. Hydrogen bond distances (Å) for (*S*)-Sn(IV).

D-H...A	d(D...A)	D-H...A	d(D...A)
O(1)-H(1O)...F(1)#2	2.703(3)	N(1)-H(2N)...F(1)#4	2.974(4)
O(3)-H(3O)...F(3)	2.558(4)	N(1)-H(3N)...O(1)#5	2.888(4)
N(1)-H(2N)...O(2)#3	2.749(4)	N(1)-H(1N)...F(2)#6	2.826(4)

Symmetry operation: #1 -x+1,-y+2,z #2 -x+1,-y+1,z-1 #3 -x+1/2,y-1/2,-z+2
#4 -x+1,-y+1,z #5 -x+1/2,y-1/2,-z+1 #6 x-1/2,-y+3/2,-z+2

Fig. S3 TGA diagrams for (a) (*R*)-Sn(II)/(*S*)-Sn(II) and (b) (*R*)-Sn(IV)/(*S*)-Sn(IV).

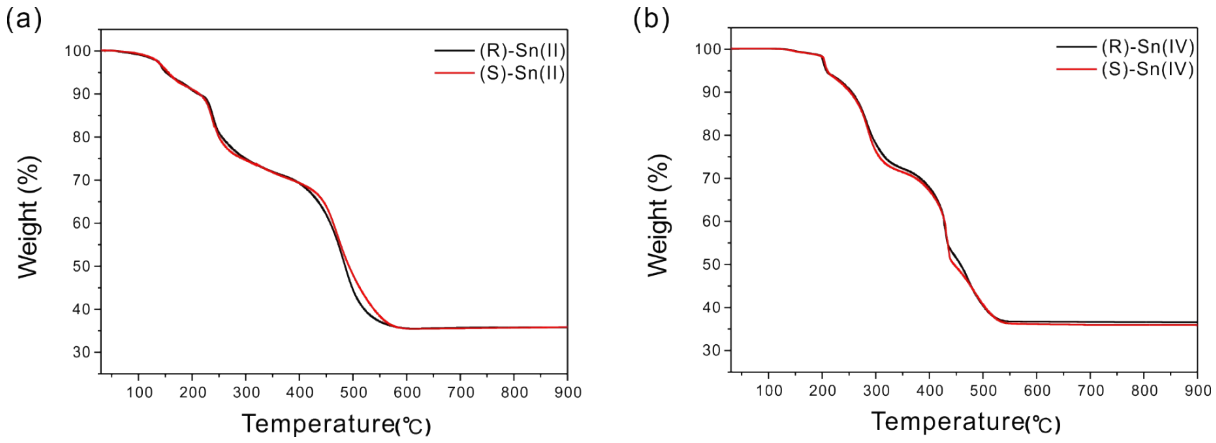

Fig. S4 PXRD patterns measured after heating the samples to 700 °C.

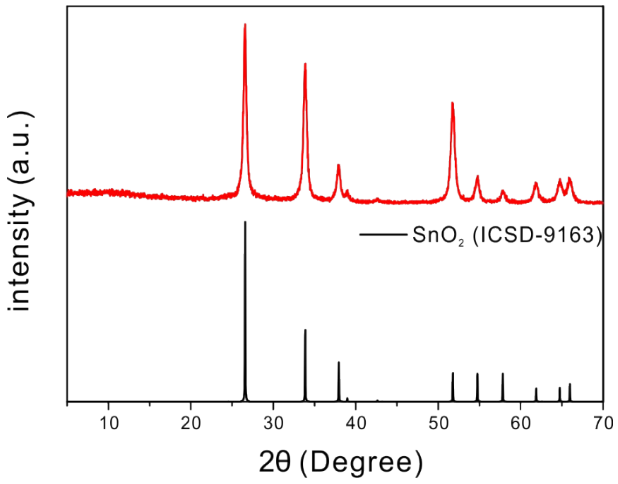

Table S10. EA data for (*R*)-Sn(II), (*S*)-Sn(II), (*R*)-Sn(IV), and (*S*)-Sn(IV).

Element	Calculated	Experimental	
		(*R*)-Sn(II)	(*S*)-Sn(II)
N	4.07	3.91	3.95
C	27.92	27.02	27.54
H	2.91	2.96	2.88
Totals	34.90	33.89	34.37

Element	Calculated	Experimental	
		(*R*)-Sn(IV)	(*S*)-Sn(IV)
N	4.92	4.81	4.84
C	33.74	33.63	33.74
H	3.51	3.64	3.63
Totals	42.17	42.09	42.21

Fig. S5 UV-vis diffuse reflectance spectra for D-HPG, L-HPG, (*R*)-Sn(II), (*S*)-Sn(II), (*R*)-Sn(IV), and (*S*)-Sn(IV).

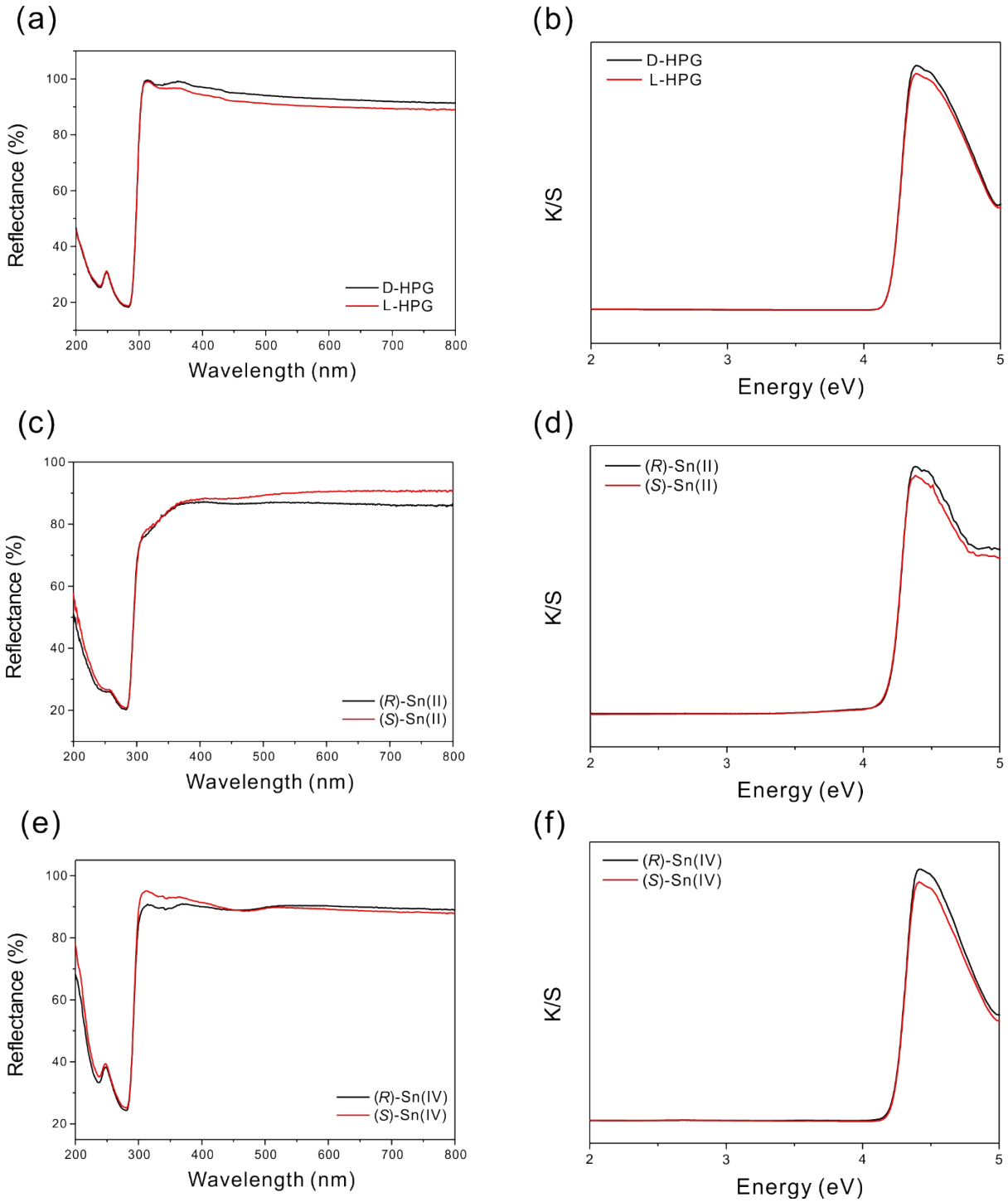

Fig. S6 IR spectra for (*R*)-Sn(II), (*S*)-Sn(II), (*R*)-Sn(IV), and (*S*)-Sn(IV).

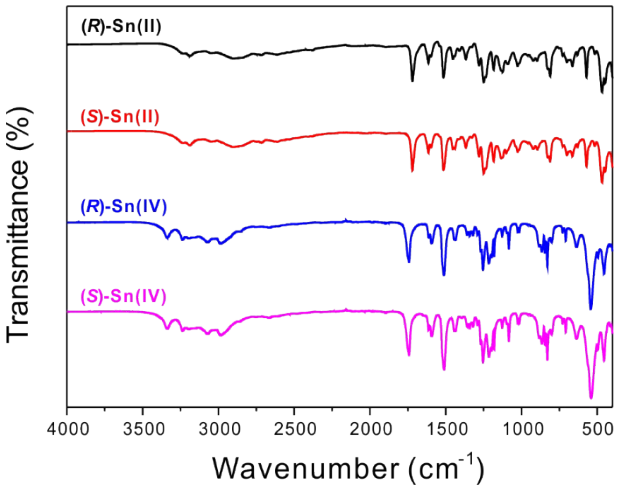

Table S11. Calculated dipole moments of (*R*)-Sn(II) and (*R*)-Sn(IV) (D = Debye).

Compound	Unit	Magnitude	Dipole moment (D)		
			x	***y***	***z***
(*R*)-Sn(II)	SnF_3(1)	7.47 D	-6.7	-3.2	-0.79
	SnF_3(2)	7.47 D	6.7	-3.2	0.79
	SnF_3(3)	7.62 D	6.48	3.79	-1.28
	SnF_3(4)	7.62 D	-6.48	3.79	1.28
	Net	**1.18 D**	**0**	**1.18**	**0**
(*R*)-Sn(IV)	SnF_6(1)	8.58 D	-3.55×10^{-15}	-7.11×10^{-15}	8.58
	SnF_6(2)	8.58 D	1.60×10^{-14}	-2.97×10^{-13}	8.58
	SnF_6(3)	8.58 D	-1.78×10^{-15}	5.33×10^{-15}	-8.58
	SnF_6(4)	8.58 D	-1.24×10^{-14}	5.33×10^{-15}	-8.58
	Net	**0 D**	**0**	**0**	**0**

Fig. S7 Dipole moments and a net direction of SnF_3 trigonal pyramids in a unit cell for (*R*)-Sn(II).

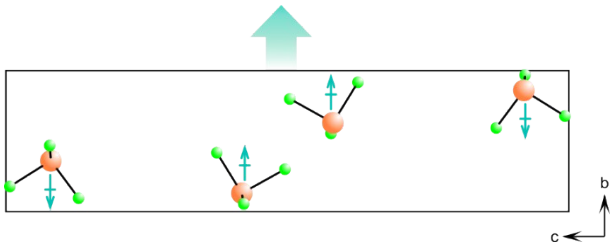

Fig. S8 Dipole moments and a net direction of SnF_6 octahedra in a unit cell for (*R*)-Sn(IV).

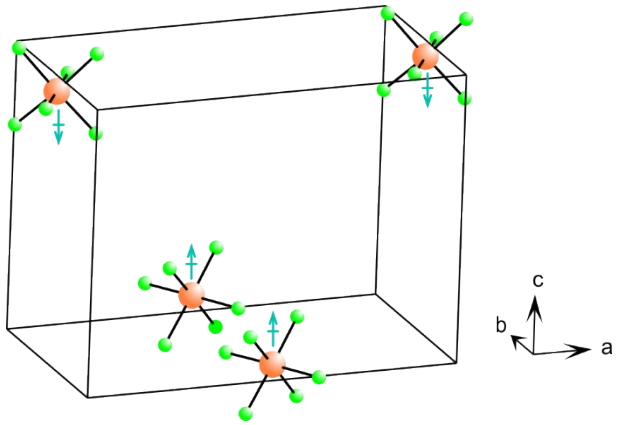

Table S12. The calculated distortion of $[SnF_6]^{2-}$ octahedron for (*R*)-Sn(IV)**.**

Distance(Å)		Angle(°)	
Sn-F1	1.9608	∠F1 Sn F4	179.29
Sn-F2	1.9448	∠F2 Sn F5	174.53
Sn-F3	1.9448	∠F3 Sn F6	174.53
Sn-F4	1.9609		
Sn-F5	1.9680		
Sn-F6	1.9680		
			Δd=0.0467

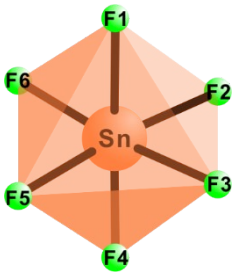

Fig. S9 Solid-state CD spectra of D-HPG, L-HPG, (*R*)-Sn(II), (*S*)-Sn(II), (*R*)-Sn(IV), and (*S*)-Sn(IV).

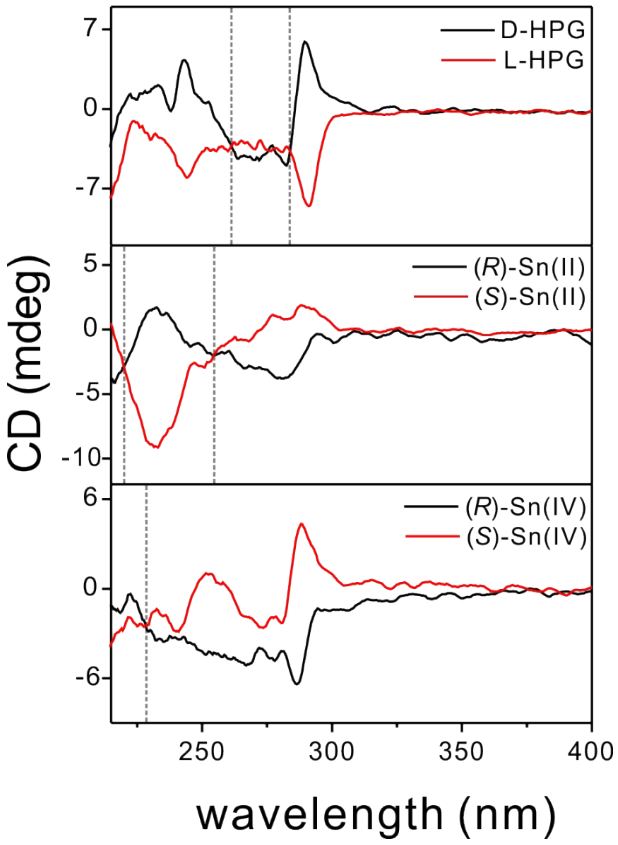

Fig. S10 Band structures for (a) (*R*)-Sn(II), (b) (*S*)-Sn(II), (c) (*R*)-Sn(IV), and (d) (*S*)-Sn(IV).

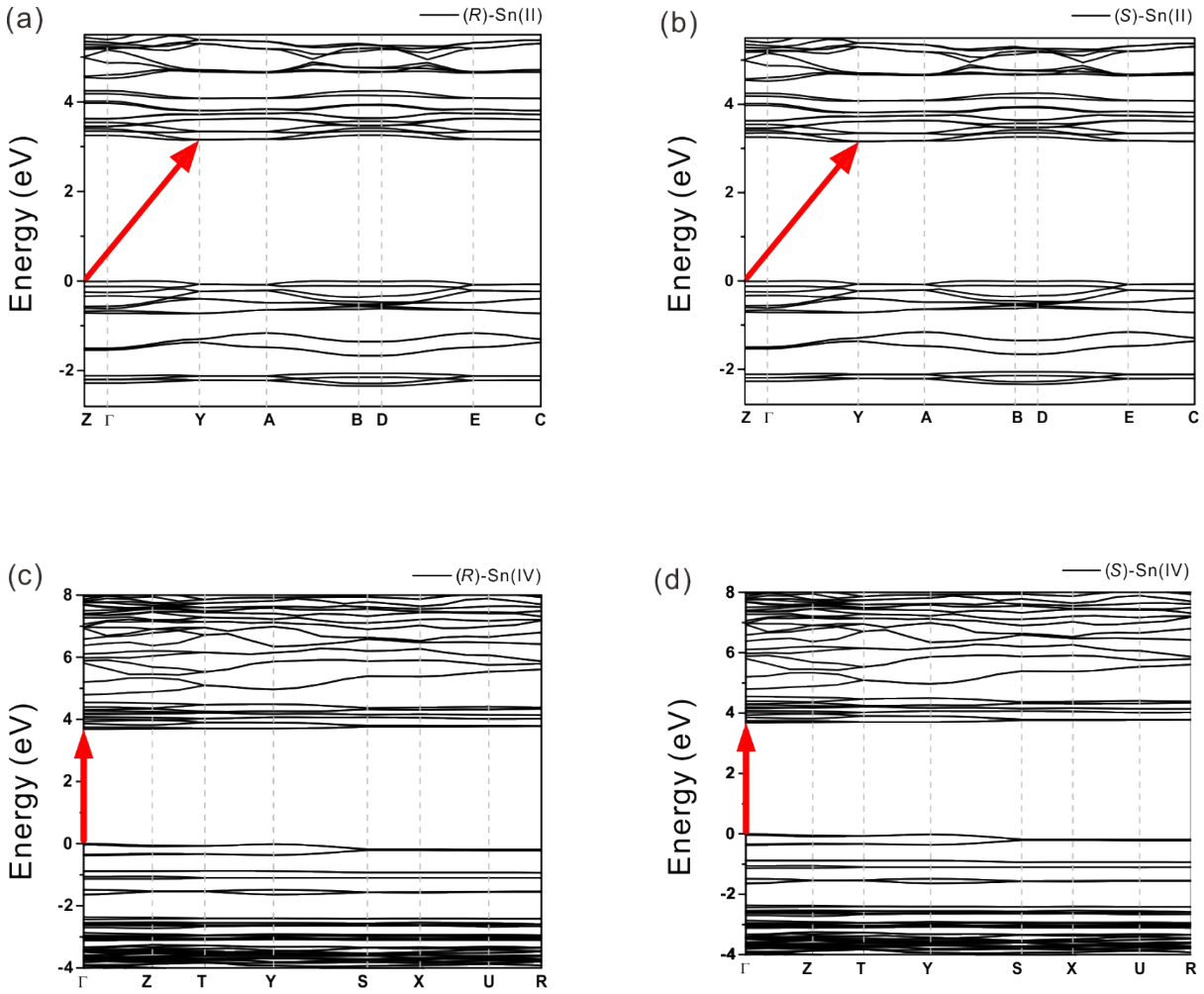

Fig. S11 Total and partial density of states for (a) (*R*)-Sn(II), (b) (*S*)-Sn(II), (c) (*R*)-Sn(IV), and (d) (*S*)-Sn(IV).

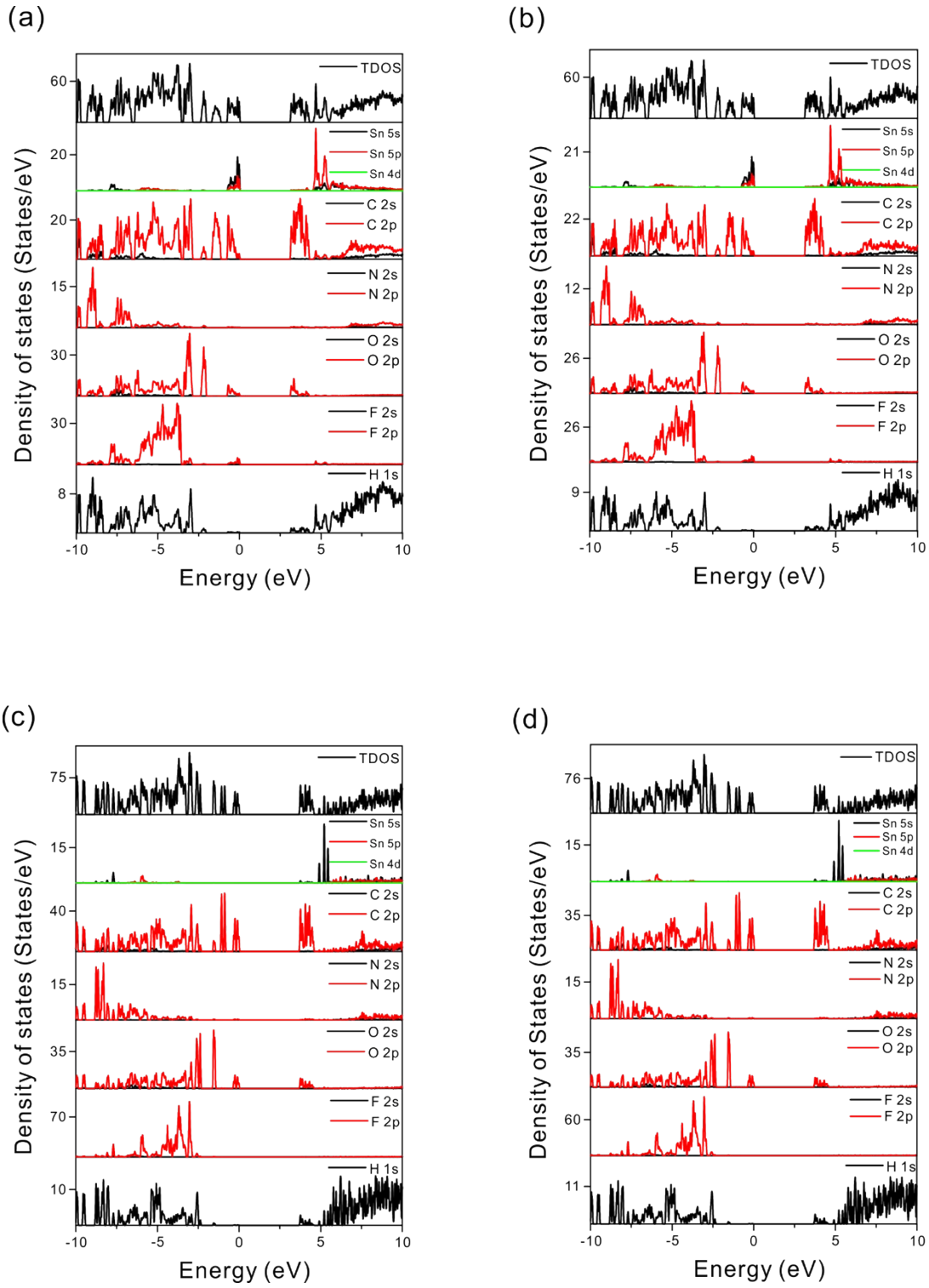

Fig. S12 PXRD patterns revealing the stability of (*R*)-Sn(IV) in various solvents.