Supporting Information

Chiral-Driven Formation of Hybrid Cyanurates with Large Birefringence

*Yue Zhao [a,b,c], Chunli Hu [a], Pengfei Chen [a,b,c], Mingzhi Zhang [a,c] and Jianggao Mao [*a,b,c]*

a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China.

b School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, P. R. China

c University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

* Corresponding Authors: mjg@fjirsm.ac.cn

Table of Contents

Table S1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *rac*-*α*-MBACY, *R*-*α*-MBACY and *S*-*α*-MBACY. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
		rac-*α*-MBACY		
C(1)	5519.0(8)	7956.2(17)	3957.0(10)	31.9(3)
C(2)	6046.4(7)	4809.5(17)	4815.2(9)	27.3(2)
C(3)	6367.4(7)	7751.0(18)	5882.7(10)	29.2(3)
C(4)	8325.8(9)	2669(2)	7333.3(11)	43.2(3)
C(5)	8806.1(11)	924(3)	7366.9(15)	58.7(4)
C(6)	9427.3(13)	699(4)	6651.9(18)	74.6(6)
C(7)	9565.7(12)	2185(4)	5892.9(17)	76.9(6)
C(8)	9086.0(13)	3918(4)	5824.6(16)	73.3(6)
C(9)	8468.3(10)	4175(3)	6550.6(14)	56.9(4)
C(10)	7684.6(8)	2924(2)	8166.7(11)	38.9(3)
C(11)	7760.8(10)	4913(3)	8824.1(14)	55.6(4)
O(1)	5124.2(8)	8930.3(15)	3159.3(8)	53.0(3)
O(2)	6097.3(6)	2961.9(12)	4669.8(7)	39.1(2)
O(3)	6725.7(7)	8692.8(13)	6736.4(8)	43.8(3)
N(1)	5912.6(7)	8813.0(14)	4961.8(8)	31.7(2)
N(2)	5601.2(7)	5926.2(14)	3920.0(8)	31.8(2)
N(3)	6410.2(6)	5732.0(14)	5795.3(8)	30.7(2)
N(4)	6803.0(6)	2726.1(15)	7522.6(8)	33.2(2)
		R-*α*-MBACY		
C(1)	3724(4)	4202(2)	-1064(2)	40.7(6)
C(2)	3866(3)	6013(2)	-315.9(19)	36.6(5)
C(3)	4784(3)	4576(2)	799.4(18)	34.1(5)
C(4)	10643(3)	5285(2)	6207.8(18)	35.9(5)
C(5)	10690(3)	3428(2)	5570(2)	38.7(6)

C(6)	9230(4)	4711(2)	4483(2)	41.5(6)
C(7)	4503(4)	6380(2)	4484(2)	44.1(6)
C(8)	4843(6)	5492(3)	5129(3)	68.9(10)
C(9)	5197(6)	5604(4)	6244(3)	84.1(13)
C(10)	5174(4)	6601(4)	6709(2)	67.2(10)
C(11)	4806(5)	7477(3)	6086(3)	64.2(9)
C(12)	4473(5)	7370(3)	4979(3)	59.1(8)
C(13)	4156(4)	6248(3)	3275(2)	47.2(6)
C(14)	2748(5)	6967(5)	2737(3)	87.6(15)
C(15)	9294(4)	4071(3)	740(2)	51.8(7)
C(16)	9105(5)	3772(4)	-344(3)	71.9(10)
C(17)	8702(7)	4539(6)	-1137(4)	99.5(18)
C(18)	8457(6)	5570(5)	-881(4)	98.2(18)
C(19)	8619(6)	5888(4)	188(5)	91.3(15)
C(20)	9061(5)	5130(3)	1002(3)	66.6(9)
C(21)	9739(4)	3216(3)	1593(2)	48.0(6)
C(22)	11437(4)	3403(4)	2277(3)	75.6(11)
O(1)	3388(3)	3577.2(17)	-1825.0(16)	62.9(7)
O(2)	3671(3)	6974.2(15)	-541.8(16)	51.9(5)
O(3)	5324(2)	4184.2(16)	1682.6(13)	42.2(4)
O(4)	11046(3)	5964.3(15)	6909.5(14)	46.9(5)
O(5)	11259(3)	2521.2(16)	5787.7(16)	52.6(5)
O(6)	8353(3)	4999.5(17)	3628.1(15)	57.7(6)
N(1)	4460(3)	3878.7(17)	-76.3(17)	40.2(5)
N(2)	3374(3)	5267.4(17)	-1139.0(17)	41.1(5)
N(3)	4512(3)	5639.0(18)	653.7(16)	38.0(5)
N(4)	9703(3)	5505.8(17)	5249.1(16)	38.8(5)
N(5)	11084(3)	4229.0(17)	6342.6(17)	42.5(5)
N(6)	9710(3)	3689.9(19)	4653.8(17)	45.4(5)

N(7)	5763(3)	6443.9(18)	2761.6(16)	40.3(5)
N(8)	8382(3)	3129.8(17)	2321.6(16)	35.1(4)
		S-*α*-MBACY		
C(1)	13723(3)	5797.5(17)	-1061.1(15)	41.1(4)
C(2)	14784(2)	5419.1(17)	800.8(14)	34.7(4)
C(3)	13868(2)	3984.7(16)	-318.8(14)	37.2(4)
C(4)	10643(2)	4711.6(16)	6209.6(14)	35.8(4)
C(5)	9233(3)	5285.4(18)	4481.2(15)	41.4(4)
C(6)	10689(3)	6568.5(16)	5569.9(15)	39.0(4)
C(7)	14503(3)	3618(2)	4485.0(16)	44.8(5)
C(8)	14468(4)	2626(2)	4978(2)	59.4(6)
C(9)	14808(4)	2521(3)	6087(2)	65.7(7)
C(10)	15169(3)	3399(3)	6709.8(19)	68.3(8)
C(11)	15197(5)	4389(3)	6245(2)	83.8(10)
C(12)	14849(5)	4506(3)	5128(2)	69.6(7)
C(13)	14156(3)	3750(2)	3273.6(16)	47.9(5)
C(14)	12742(4)	3034(4)	2737(2)	88.8(12)
C(15)	9298(3)	5930(2)	743.2(19)	52.3(5)
C(16)	9058(4)	4866(3)	1000(3)	67.5(7)
C(17)	8615(5)	4109(3)	183(4)	92.7(12)
C(18)	8459(5)	4428(4)	-883(3)	99.2(15)
C(19)	8710(5)	5468(5)	-1139(3)	99.0(15)
C(20)	9106(4)	6227(3)	-343(2)	74.4(9)
C(21)	9740(3)	6783(2)	1592.3(18)	48.3(5)
C(22)	11441(3)	6595(3)	2278(3)	77.0(9)
O(1)	13388(3)	6420.8(14)	-1824.9(13)	63.1(5)
O(2)	15324.1(18)	5810.6(13)	1684.3(10)	42.8(3)
O(3)	13668(2)	3021.2(12)	-542.1(12)	52.1(4)
O(4)	11046(2)	4031.3(12)	6909.5(11)	47.6(4)

O(5)	8353(2)	4996.0(15)	3627.8(12)	58.5(5)
O(6)	11258(2)	7476.6(13)	5787.2(12)	53.3(4)
N(1)	13376(2)	4729.7(14)	-1140.1(12)	41.4(4)
N(2)	14458(2)	6117.6(14)	-75.4(13)	40.1(4)
N(3)	14510(2)	4358.4(15)	653.3(12)	38.4(4)
N(4)	11084(2)	5766.8(14)	6343.3(13)	42.7(4)
N(5)	9702(2)	4489.4(14)	5246.1(12)	39.0(4)
N(6)	9713(2)	6306.2(15)	4651.5(14)	45.6(4)
N(7)	15765(2)	3551.7(15)	2760.8(12)	40.6(4)
N(8)	8382(2)	6867.5(14)	2321.0(12)	35.0(3)

Table S2. Selected bond lengths (Å) for *rac*-*α*-MBACY, *R*-*α*-MBACY and *S*-*α*-MBACY.

Atom-Atom	Length/ Å	Atom-Atom	Length/ Å
rac-*α*-MBACY			
C(4)-C(5)	1.387(2)	O(2)-C(2)	1.2436(15)
C(4)-C(9)	1.389(2)	O(3)-C(3)	1.2339(14)
C(4)-C(10)	1.5123(19)	N(1)-C(1)	1.3592(15)
C(5)-C(6)	1.387(3)	N(1)-C(3)	1.3881(14)
C(6)-C(7)	1.359(3)	N(2)-C(1)	1.3569(15)
C(7)-C(8)	1.379(3)	N(2)-C(2)	1.3807(14)
C(8)-C(9)	1.394(3)	N(3)-C(2)	1.3407(15)
C(10)-C(11)	1.520(2)	N(3)-C(3)	1.3482(16)
O(1)-C(1)	1.2216(15)	N(4)-C(10)	1.4978(16)
R-*α*-MBACY			
C(7)-C(8)	1.372(5)	O(3)-C(3)	1.233(3)
C(7)-C(12)	1.376(4)	O(4)-C(4)	1.229(3)
C(7)-C(13)	1.509(4)	O(5)-C(5)	1.229(3)
C(8)-C(9)	1.393(5)	O(6)-C(6)	1.251(3)
C(10)-C(9)	1.367(7)	N(1)-C(1)	1.357(3)
C(10)-C(11)	1.348(6)	N(1)-C(3)	1.393(3)
C(11)-C(12)	1.380(4)	N(2)-C(1)	1.352(3)
C(13)-C(14)	1.514(5)	N(2)-C(2)	1.402(3)
C(15)-C(16)	1.393(5)	N(3)-C(2)	1.338(3)
C(15)-C(20)	1.372(6)	N(3)-C(3)	1.345(3)
C(15)-C(21)	1.514(4)	N(4)-C(4)	1.357(3)
C(16)-C(17)	1.382(6)	N(4)-C(6)	1.392(3)
C(17)-C(18)	1.338(9)	N(5)-C(4)	1.361(3)
C(18)-C(19)	1.382(7)	N(5)-C(5)	1.394(3)
C(19)-C(20)	1.397(5)	N(6)-C(5)	1.340(3)
C(21)-C(22)	1.513(4)	N(6)-C(6)	1.333(4)

O(1)-C(1)	1.230(3)	N(7)-C(13)	1.499(4)
O(2)-C(2)	1.231(3)	N(8)-C(21)	1.482(4)
S-α-MBACY			
C(7)-C(8)	1.378(4)	O(3)-C(3)	1.234(3)
C(7)-C(12)	1.371(4)	O(4)-C(4)	1.229(2)
C(7)-C(13)	1.513(3)	O(5)-C(5)	1.251(2)
C(8)-C(9)	1.383(3)	O(6)-C(6)	1.231(3)
C(9)-C(10)	1.349(5)	N(1)-C(1)	1.354(3)
C(10)-C(11)	1.360(6)	N(1)-C(3)	1.400(2)
C(11)-C(12)	1.395(4)	N(2)-C(1)	1.355(2)
C(13)-C(14)	1.515(4)	N(2)-C(2)	1.395(2)
C(15)-C(16)	1.376(5)	N(3)-C(2)	1.343(3)
C(15)-C(20)	1.395(4)	N(3)-C(3)	1.340(2)
C(15)-C(21)	1.509(3)	N(4)-C(4)	1.360(3)
C(16)-C(17)	1.400(4)	N(4)-C(6)	1.395(3)
C(17)-C(18)	1.379(6)	N(5)-C(4)	1.362(2)
C(18)-C(19)	1.349(8)	N(5)-C(5)	1.392(2)
C(19)-C(20)	1.378(5)	N(6)-C(5)	1.331(3)
C(21)-C(22)	1.516(3)	N(6)-C(6)	1.341(2)
O(1)-C(1)	1.231(2)	N(7)-C(13)	1.500(3)
O(2)-C(2)	1.233(2)	N(8)-C(21)	1.483(3)

Table S3. Hydrogen bond lengths (Å) for *rac*-α-MBACY, *R*-α-MBACY and *S*-α-MBACY.

D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
rac-α-MBACY				
N(1)-H(1)···O(2)^{2}	0.86	1.99	2.7988(13)	156
N(2)-H(2)···O(1)^{1}	0.86	1.98	2.8343(13)	176.3
N(4)-H(4A)···N(3)	0.89	1.94	2.8254(14)	174.9
N(4)-H(4C)···O(3)^{3}	0.89	1.96	2.8266(14)	165.1
R-α-MBACY				
N(1)-H(1)···O(2)^{2}	0.86	2.04	2.840(3)	154.6
N(4)-H(4)···O(5)^{1}	0.86	2.06	2.875(3)	158.7
N(5)-H(5)···O(1)^{3}	0.86	2.01	2.859(3)	167.7
N(7)-H(7A)···N(3)	0.89	2.02	2.875(3)	161.6
N(7)-H(7B)···O(6)	0.89	1.95	2.827(3)	169.8
N(8)-H(8A)···O(3)	0.89	2.14	2.766(3)	126.4
N(8)-H(8B)···O(6)	0.89	1.95	2.836(3)	176.3
N(8)-H(8C)···O(4)^{4}	0.89	2.05	2.871(3)	153.1
S-α-MBACY				
N(2)-H(2)···O(3)^{2}	0.86	2.04	2.840(2)	154.6
N(4)-H(4)···O(1)^{5}	0.86	2.01	2.859(2)	167.7
N(5)-H(5)···O(6)^{1}	0.86	2.05	2.871(2)	158.9
N(7)-H(7A)···N(3)	0.89	2.02	2.876(2)	161.4
N(7)-H(7C)···O(5)^{6}	0.89	1.95	2.826(2)	169.9
N(8)-H(8A)···O(2)^{3}	0.89	2.16	2.766(2)	124.4
N(8)-H(8B)···O(4)^{4}	0.89	2.06	2.869(2)	151
N(8)-H(8C)···O(5)	0.89	1.95	2.839(2)	174.1

Symmetry transformations used to generate equivalent atoms:

rac-α-MBACY: ^{1}1-X,-1/2+Y,1/2-Z; ^{2}+X,1+Y,+Z; ^{3}+X,-1+Y,+Z

R-α-MBACY: ^{1}2-X,1/2+Y,1-Z; ^{2}1-X,-1/2+Y,-Z; ^{3}1+X, +Y,1+Z; ^{4}2-X,-1/2+Y,1-Z

S-α-MBACY: ^{1}2-X,-1/2+Y,1-Z; ^{2}3-X,1/2+Y,-Z; ^{3}-1+X, +Y,+Z; ^{4}2-X,1/2+Y,1-Z; ^{5}+X, +Y,1+Z; ^{6}1+X, +Y,+Z

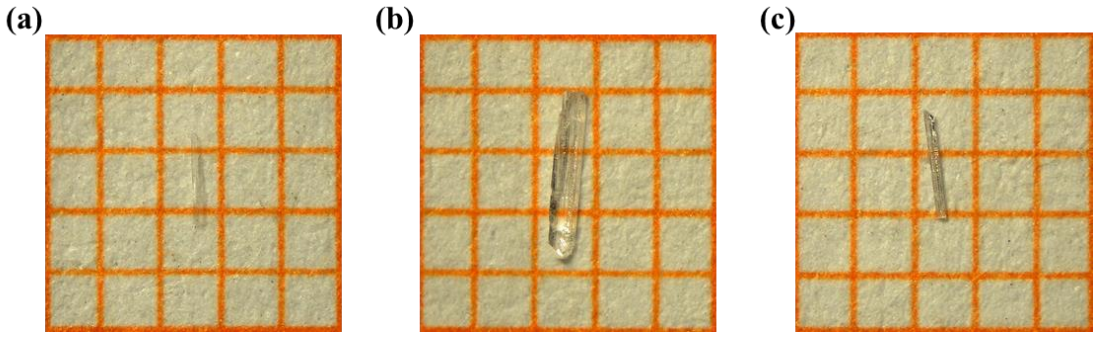

Figure S1. The photographs of crystals for *rac*-*α*-MBACY (a), *R*-*α*-MBACY (b) and *S*-*α*-MBACY(c).

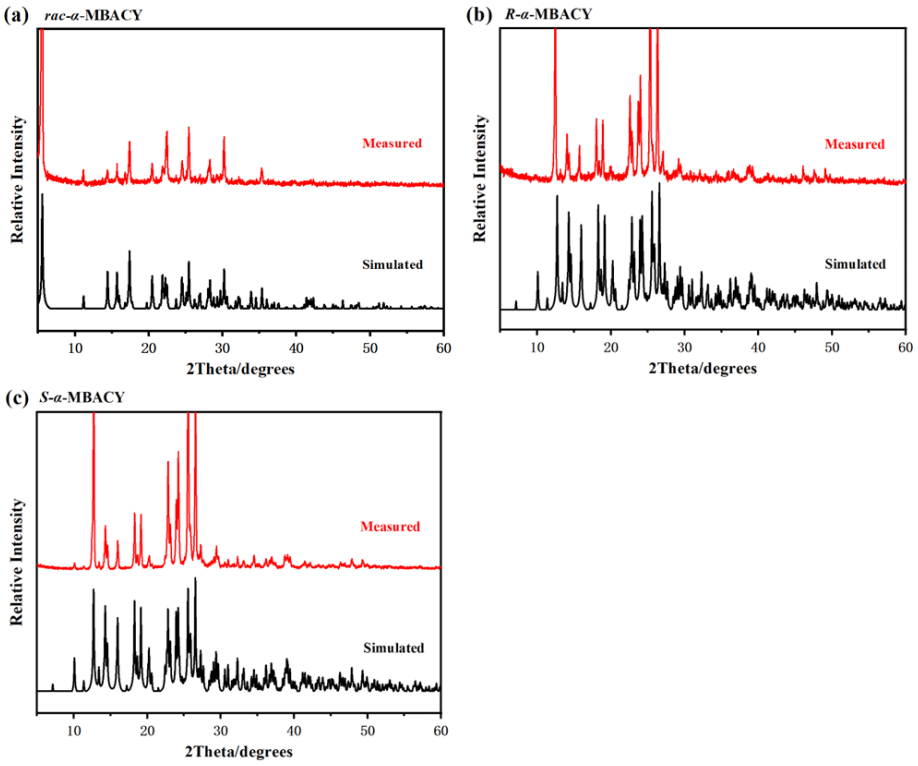

Figure S2. Simulated and experimental powder X-ray diffraction patterns of *rac*-*α*-MBACY (a), *R*-*α*-MBACY (b) and *S*-*α*-MBACY(c).

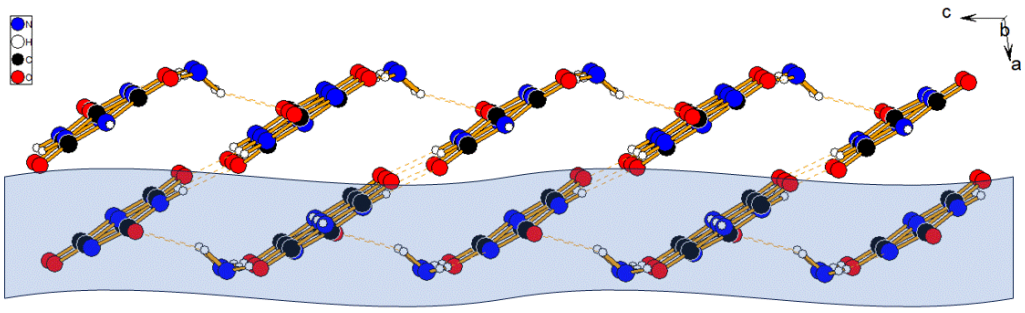

Figure S3. A double hydrogen-bonded layer parallel to the *bc*-plane in *rac*-*α*-MBACY. The highlighted area in the figure corresponds the single hydrogen bonded layer as represented in Fig 1b.

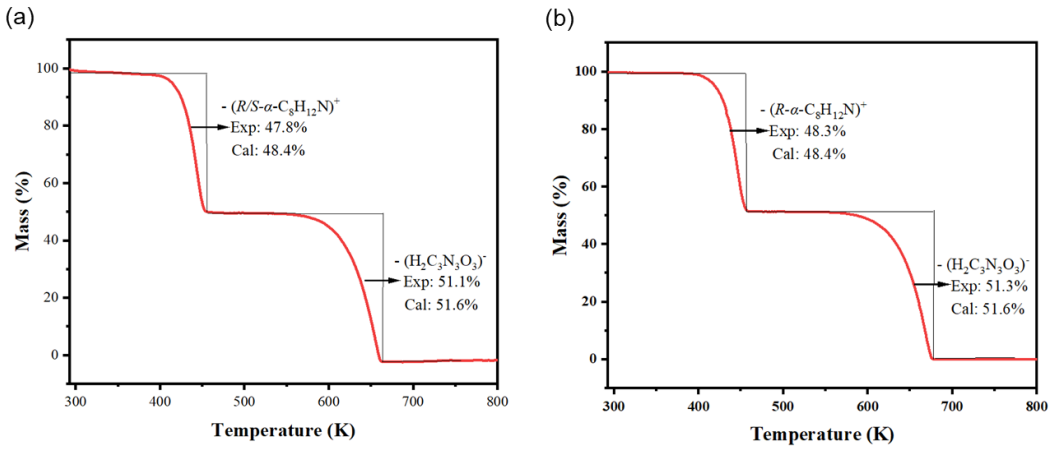

Figure S4. The TGA curves of *rac*-*α*-MBACY (a) and *R*-*α*-MBACY (b) under N_2 atmosphere.

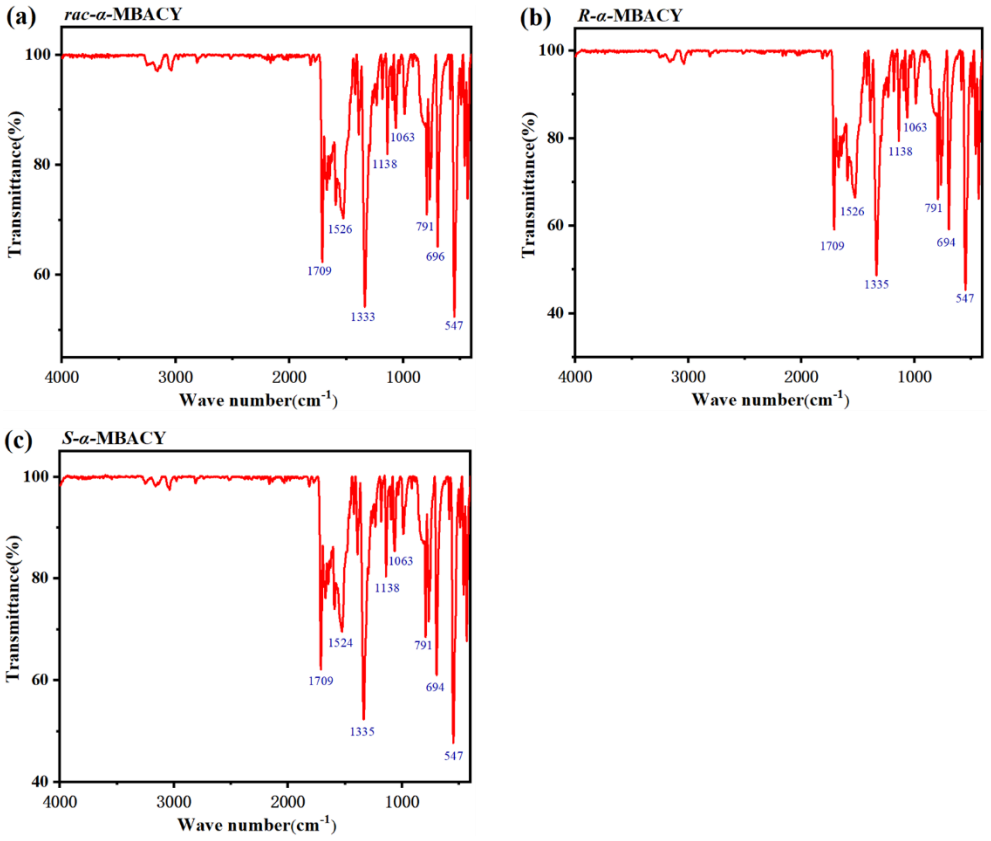

Figure S5. The IR spectra of *rac*-α-MBACY (a), *R*-α-MBACY (b) and *S*-α-MBACY(c).

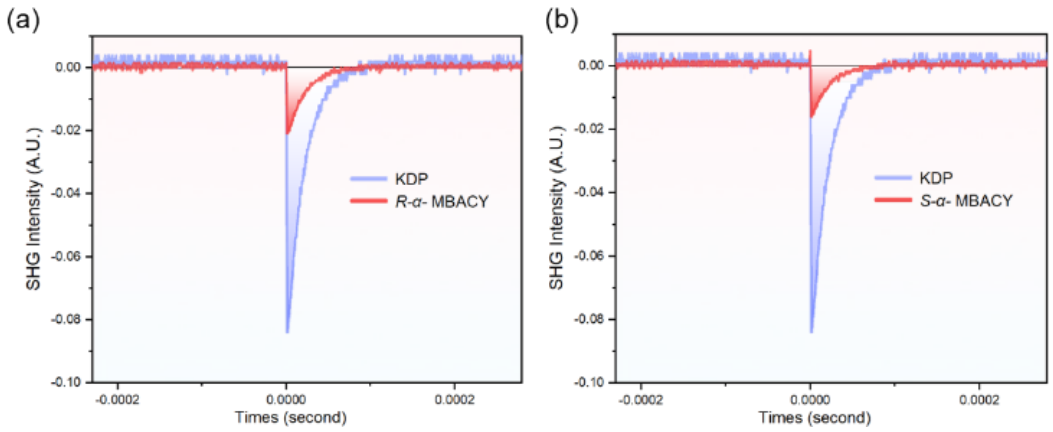

Figure S6. The SHG signals of *R*-α-MBACY (a) and *S*-α-MBACY (b) compared with KDP as the standard.

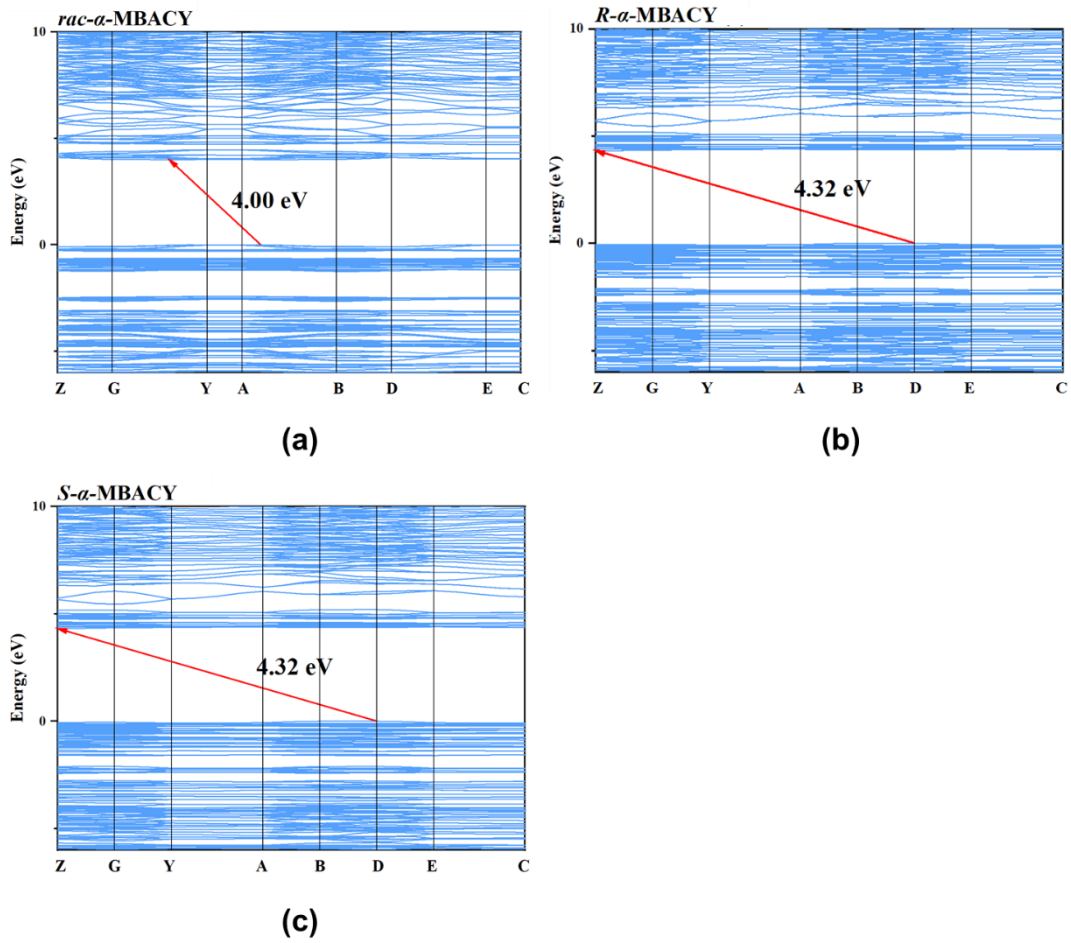

Figure S7. The electronic band structures of *rac*-*α*-MBACY (a), *R*-*α*-MBACY (b) and *S*-*α*-MBACY (c).

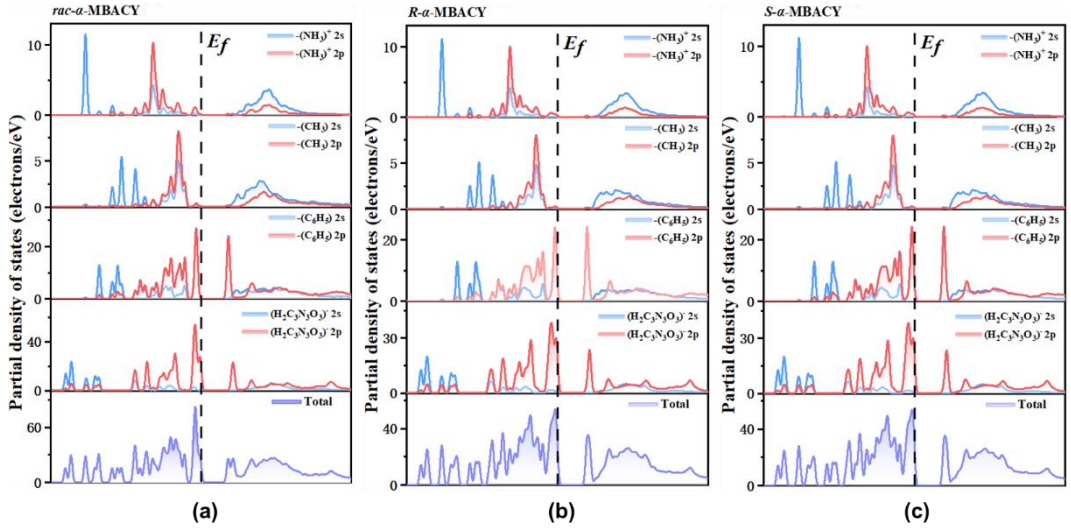

Figure S8. Total and partial density of states for *rac*-*α*-MBACY (a), *R*-*α*-MBACY (b) and *S*-*α*-MBACY(c).