Asymmetry-Driven Organic-Inorganic Hybrid Strategy for Constructing Structures with Exceptional Organofunctionalized B-O Units

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Synthesis

Colorless and transparent single crystals of $[C(NH_2)_3]_2(CH_3)_4B_4O_5{\cdot}2H_2O$ (GCHBO) were obtained by a slow evaporation method from an aqueous solution. $CH_3B(OH)_2$ and $NH_2C(=NH)NH_2{\cdot}1/2H_2CO_3$ were mixed thoroughly in a molar ratio of 4:1 and placed in a clean beaker. Subsequently, 20 mL of deionized water was added, and the mixture was stirred magnetically for 10 minutes to ensure complete dissolution. The beaker was then sealed with plastic film to minimize contamination and evaporation. The solution was maintained in a water bath at 60 °C for one week to promote slow evaporation and crystal growth. After heating, large colorless GCHBO single crystals were obtained. To prepare polycrystalline powder samples, the as-grown crystals were collected and finely ground. Phase purity of the obtained powder was confirmed by X-ray diffraction (XRD) analysis.

Polycrystalline samples of $Rb_2(CH_3)_4B_4O_5{\cdot}4H_2O$ (RCHBO) and $Li(CH_3)_4B_4O_3(OH)_3$ (LCHBO) were synthesized via a room-temperature solution method. Rb_2CO_3 and $CH_3B(OH)_2$, as well as LiOH and $CH_3B(OH)_2$, were mixed thoroughly in a molar ratio of 1:4 and placed in clean beakers. Subsequently, 20 mL of deionized water was added to each mixture, followed by magnetic stirring for 10 minutes to ensure complete dissolution. The beakers were sealed with plastic film to minimize contamination and evaporation. The resulting solutions were left undisturbed at room temperature for 15 days to allow slow evaporation. Finally, polycrystalline powder samples of RCHBO and LCHBO were obtained. The phase purity of the obtained powders was confirmed by XRD analysis.

Structure Determination

The crystal structure of RCHBO, GCHBO and LCHBO were determined using a Bruker D8 Venture single-crystal X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 293(3) K. Data collection, processing, and absorption corrections were carried out using Bruker SAINT software[1]. Structural determination was performed using the Olex2 interface[2]. Initial structure solutions were obtained via the Intrinsic Phasing method, and the models were refined through full-matrix least-squares refinement using SHELXL[3]. Potential higher symmetry elements in the structures were evaluated using the ADDSYM algorithm in the PLATON program[4]. Detailed crystallographic data and refinement parameters are summarized in Table S1, while atomic coordinates, equivalent isotropic displacement parameters, bond valence sums, bond lengths, bond angles, and hydrogen bonds are provided in Tables S2–S7.

Powder X-ray Diffraction

Powder X-ray diffraction (XRD) measurements for RCHBO, GCHBO and LCHBO were conducted at room temperature using a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). Data were collected over a 2θ range of 5~70°, with a step size of 0.02° and a fixed counting time of 1 second per step.

Thermal Analysis

Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out using a Netzsch STA 449C thermal analyzer. Approximately 10 mg of RCHBO, GCHBO, and LCHBO powder samples were placed in platinum crucibles and heated from room temperature to 500 °C at a rate of 5 °C min^{-1}. All measurements were performed under a continuous flow of nitrogen gas to ensure an inert atmosphere throughout the experiment.

Spectroscopic Measurements

The diffuse reflectance spectra of RCHBO, GCHBO and LCHBO were recorded using a Shimadzu SolidSpec-3700DUV spectrophotometer over the UV-Vis-NIR range (200–2600 nm). The infrared spectrum was obtained using a Shimadzu IR Affinity-1 Fourier transform infrared (FTIR) spectrometer, covering the 400–4000 cm^{-1} spectral range. For FTIR analysis, the sample was prepared by compressing a finely powdered mixture of RCHBO, GCHBO or LCHBO and dried KBr (purity: 99.9%) in a 1:100 ratio, creating a thin, semi-transparent compressed plate.

Computational Methods

First-principles calculations for RCHBO, GCHBO and LCHBO were performed using the CASTEP software[5]. The Perdew-Burke-Ernzerhof (PBE) functional was employed, with the exchange-correlation functional treated using the generalized gradient approximation (GGA). Norm-conserving pseudopotentials (NCPs) were utilized to model the interactions between the valence electrons and the core[6]. A plane-wave cutoff energy of 830 eV was used, and the total energy was computed using the self-consistent field (SCF) method with a convergence criterion of 5×10^{-7} eV/atom. To perform numerical integration of the Brillouin zone, a 4 × 4 × 2 Monkhorst-Pack k-point grid was applied. The valence electronic configurations for the NCPs are as follows: Rb: $4s^2 4p^6 5s^1$, Li: $2s^1$, C: $2s^2 2p^2$, B: $2s^2 2p^1$, N: $2s^2 2p^3$, O: $2s^2 2p^4$, and H: $1s^1$. Given that the GGA often underestimates the band gap, a more accurate evaluation was carried out using the HSE06 hybrid functional[7,8].

Table S1 Crystal data and structure refinements for $Rb_2(CH_3)_4B_4O_5{\cdot}4H_2O$, $[C(NH_2)_3]_2(CH_3)_4B_4O_5{\cdot}2H_2O$ and $Li(CH_3)_4B_4O_3(OH)_3$.

Empirical formula	$Rb_2(CH_3)_4B_4O_5{\cdot}4H_2O$	$[C(NH_2)_3]_2(CH_3)_4B_4O_5{\cdot}2H_2O$	$Li(CH_3)_4B_4O_3(OH)_3$
Formula weight	426.38	339.58	209.34
Temperature (K)	298	296.15	296.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/m$	$P2_1/c$
Unit cell dimensions	a = 10.217(5) Å	a = 7.6168(19) Å	a = 6.7451(9) Å
	b = 9.940(6) Å	b = 12.935(3) Å	b = 18.977(3) Å
	c = 16.779(14) Å	c = 9.397(2) Å	c = 9.1861(12) Å
	β = 107.73(2) °	β = 105.598(11) °	β = 92.260(5) °
Volume (Å^3)	1623.1(18)	891.7(4)	1174.9(3)
Z	4	4	4
Calculated density (g·cm^{-3})	1.745	1.265	1.183
Absorption coefficient (mm^{-1})	6.057	0.103	0.095
F (000)	840	364	440
Theta range for data collection	4.826 to 50.694 °	4.5 to 50.692 °	4.93 to 50.7 °
Limiting indices	$-12 \le h \le 12$,	$-9 \le h \le 9$,	$-8 \le h \le 8$,
	$-11 \le k \le 11$,	$-13 \le k \le 15$,	$-22 \le k \le 22$,
	$-20 \le l \le 20$	$-11 \le l \le 10$	$-11 \le l \le 11$
Reflections collected / unique	17738 / 2938	11450 / 1710	19887 / 2143
	[R(int) = 0.1161]	[R(int) = 0.0640]	[R(int) = 0.0830]
Completeness	99.0 %	99.9 %	99.8 %
Data / restraints / parameters	2938 / 0 / 190	1710 / 0 / 122	2143 / 3 / 151
Goodness-of-fit on F^2	1.000	1.069	1.130
Final R indices [$Fo^2>2\sigma(Fo^2)$][a]	R_1 = 0.0367, wR_2 = 0.0737	R_1 = 0.0656, wR_2 = 0.1816	R_1 = 0.0648, wR_2 = 0.1775
R indices (all data)[a]	R_1 = 0.0643, wR_2 = 0.0858	R_1 = 0.0780, wR_2 = 0.1949	R_1 = 0.0775, wR_2 = 0.1904
Largest diff. peak and hole	0.56 and −0.49 e·Å^{-3}	0.53 and −0.47 e·Å^{-3}	0.39 and −0.25 e·Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$

Table S2 Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) for $Rb_2(CH_3)_4B_4O_5·4H_2O$, $[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$ and $Li(CH_3)_4B_4O_3(OH)_3$.

Atoms	*x*	*y*	*z*	$U_{(eq)}$
$Rb_2(CH_3)_4B_4O_5·4H_2O$				
Rb(1)	3608.8(4)	5107.0(5)	6907.5(3)	40.54(15)
Rb(2)	1308.2(6)	13140.2(5)	10201.8(3)	53.17(18)
O(1)	447(3)	6591(3)	6193(2)	46.0(9)
O(2)	1794(4)	5006(4)	5265(2)	53.2(9)
O(3)	1412(3)	8622(3)	7261.7(17)	24.1(6)
O(4)	1683(3)	9857(3)	8544.3(18)	29.0(7)
O(5)	3581(3)	7532(3)	7975.3(18)	30.5(7)
O(6)	3445(3)	9970(3)	7879.5(18)	31.2(7)
O(7)	1736(3)	7432(3)	8568.3(18)	29.9(7)
O(8)	3634(3)	2203(3)	6748(2)	43.9(9)
O(9)	-212(3)	14720(3)	11021(2)	45.1(8)
B(1)	2896(5)	8689(5)	7402(3)	25.8(10)
B(2)	1066(5)	8618(5)	8051(3)	25.8(11)
B(3)	2976(5)	6988(5)	8530(3)	31.0(11)
B(4)	2831(5)	10438(5)	8443(3)	32.9(12)
C(1)	3298(5)	8637(4)	6547(3)	36.0(11)
C(2)	-576(4)	8565(5)	7886(3)	36.1(11)
C(3)	3709(5)	5814(6)	9121(4)	52.6(14)
C(4)	3493(6)	11692(5)	9009(4)	60.7(16)
$[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$				
O(1)	15851(2)	8416.4(13)	-3678.9(18)	35.9(5)
O(2)	15808(2)	8419.1(13)	-1124.5(19)	37.6(5)
O(3)	18188(3)	7500	-1855(2)	34.6(6)
O(4)	19718(4)	7500	1147(3)	52.9(8)
O(5)	20012(5)	7500	-3976(3)	71.2(11)
B(1)	17081(4)	8441(2)	-2118(3)	34.2(7)

B(2)	15260(5)	7500	-4343(4)	32.0(9)
B(3)	15198(6)	7500	-745(4)	35.0(9)
C(1)	13694(7)	7500	133(5)	59.6(12)
C(2)	13821(7)	7500	-5910(4)	54.8(11)
C(3)	18251(4)	9488(3)	-1854(3)	54.1(8)
C(4)	17312(4)	9542(2)	3018(3)	40.7(7)
N(1)	16798(4)	9965(2)	4115(3)	54.6(7)
N(2)	16726(4)	9915(2)	1679(3)	53.0(7)
N(3)	18429(4)	8742(2)	3273(3)	59.1(8)
		$Li(CH_3)_4B_4O_3(OH)_3$		
Li(1)		3010(3)	3706(5)	40.6(10)
O(1)		3745.5(11)	1684(2)	43.9(5)
O(2)		3628.6(10)	378.7(18)	35.1(5)
O(3)		3762.5(10)	3004.7(18)	36.5(5)
O(4)		3365.4(9)	1828.5(18)	33.5(5)
O(5)		2933.7(11)	5763.6(19)	40.3(5)
O(6)		2981.7(10)	8150(2)	40.3(5)
B(1)		3597.6(17)	404(3)	37.0(7)
B(2)		3781.2(17)	3002(3)	38.8(7)
B(3)		3876.8(16)	1650(3)	32.9(6)
B(4)		3337.8(17)	6903(3)	37.2(7)
C(1)		3376(2)	-969(3)	55.7(8)
C(2)		3833(2)	4443(4)	64.4(10)
C(3)		4672.9(16)	1460(4)	51.1(8)
C(4)		4154.7(17)	6760(3)	54.3(8)

Table S3 Selected bond lengths (Å) and angles (°) for $Rb_2(CH_3)_4B_4O_5·4H_2O$.

Rb(1)-O(1)	3.419(4)	Rb(2)-Rb(2)#4	4.491(2)
Rb(1)-O(2)	2.816(4)	B(1)-O(3)	1.463(5)
Rb(1)-O(5)	3.009(3)	B(1)-O(5)	1.526(6)
Rb(1)-O(6)#2	2.925(3)	B(1)-O(6)	1.518(5)
Rb(1)-O(8)	2.900(4)	B(1)-C(1)	1.609(6)
Rb(1)-B(1)	3.777(5)	B(2)-O(3)	1.471(5)
Rb(1)-B(1)#2	3.683(5)	B(2)-O(4)	1.511(6)
Rb(1)-B(3)	3.521(5)	B(2)-O(7)	1.500(6)
Rb(1)-C(2)#3	3.567(4)	B(2)-C(2)	1.617(6)
Rb(1)-Rb(2)#1	4.476(2)	B(3)-O(5)	1.376(6)
Rb(2)-O(1)#6	2.917(4)	B(3)-O(7)	1.362(5)
Rb(2)-O(2)#5	3.163(4)	B(3)-C(3)	1.566(7)
Rb(2)-O(8)#5	2.956(4)	B(4)-O(4)	1.364(6)
Rb(2)-O(9)	2.840(3)	B(4)-O(6)	1.366(5)
Rb(2)-O(9)#4	2.930(4)	B(4)-C(4)	1.588(7)
O(3)-B(1)-O(5)	108.7(3)	O(5)-B(1)-C(1)	110.2(3)
O(3)-B(1)-O(6)	108.8(3)	O(5)-B(3)-C(3)	119.6(4)
O(3)-B(1)-C(1)	112.9(4)	O(6)-B(1)-O(5)	105.9(3)
O(3)-B(2)-O(4)	108.5(3)	O(6)-B(1)-C(1)	110.1(3)
O(3)-B(2)-O(7)	109.3(3)	O(6)-B(4)-C(4)	118.7(4)
O(3)-B(2)-C(2)	111.6(4)	O(7)-B(2)-O(4)	106.4(3)
O(4)-B(4)-O(6)	122.4(4)	O(7)-B(2)-C(2)	109.9(3)
O(4)-B(2)-C(2)	111.0(3)	O(7)-B(3)-O(5)	121.4(4)
O(4)-B(4)-C(4)	118.9(4)	O(7)-B(3)-C(3)	119.0(4)

Symmetry transformations used to generate equivalent atoms:

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

Table S4 Selected bond lengths (Å) and angles (°) for $[C(NH_2)_3]_2(CH_3)_4B_4O_5 \cdot 2H_2O$.

B(1)-O(1)	1.514(3)	B(2)-C(2)	1.582(5)
B(1)-O(2)	1.516(3)	B(2)#1-C(2)	1.582(5)
B(1)-O(3)	1.463(3)	B(3)-O(2)	1.359(3)
B(1)#1-O(3)	1.463(3)	B(3)-O(2)#1	1.359(3)
B(1)-C(3)	1.603(4)	B(3)-C(1)	1.582(5)
B(2)-O(1)	1.359(3)	N(1)-C(4)	1.316(4)
B(2)#1-O(1)	1.359(3)	N(2)-C(4)	1.308(3)
B(2)-O(1)#1	1.359(3)	N(3)-C(4)	1.321(4)
N(1)-C(4)-N(3)	119.7(3)	O(2)-B(1)-C(3)	110.0(2)
N(2)-C(4)-N(1)	120.3(3)	O(2)-B(3)-O(2)#1	122.1(3)
N(2)-C(4)-N(3)	120.0(3)	O(2)-B(3)-C(1)	118.93(16)
O(1)-B(1)-O(2)	105.4(2)	O(2)#1-B(3)-C(1)	118.93(16)
O(1)-B(1)-C(3)	110.0(2)	O(3)-B(1)-O(1)	108.9(2)
O(1)#1-B(2)-O(1)	121.5(3)	O(3)-B(1)-O(2)	108.4(2)
O(1)-B(2)-C(2)	119.24(16)	O(3)-B(1)-C(3)	113.9(2)
O(1)#1-B(2)-C(2)	119.25(16)		

Symmetry transformations used to generate equivalent atoms:

#1 x, 3/2-y, z

Table S5 Selected bond lengths (Å) and angles (°) for $Li(CH_3)_4B_4O_3(OH)_3$.

Li(1)-O(3)	1.985(5)	B(3)-O(2)	1.501(3)
Li(1)-O(4)	1.987(5)	B(3)-O(3)	1.507(3)
Li(1)-O(5)	1.919(5)	B(3)-O(4)	1.491(3)
Li(1)#1-O(5)	1.968(5)	B(4)-O(5)	1.362(4)
Li(1)-O(6)#2	1.968(5)	B(4)-O(6)	1.369(4)
B(1)-O(1)	1.390(4)	C(1)-B(1)	1.567(4)
B(1)-O(2)	1.348(3)	C(2)-B(2)	1.568(4)
B(2)-O(1)	1.390(4)	C(3)-B(3)	1.592(4)
B(2)-O(3)	1.348(4)	C(4)-B(4)	1.557(5)
O(1)-B(1)-C(1)	118.1(2)	O(3)-B(3)-C(3)	112.9(2)
O(1)-B(2)-C(2)	118.5(2)	O(4)-B(3)-O(2)	106.9(2)
O(2)-B(3)-O(3)	107.37(19)	O(4)-B(3)-O(3)	103.1(2)
O(2)-B(3)-C(3)	111.9(2)	O(4)-B(3)-C(3)	114.1(2)
O(2)-B(1)-O(1)	120.0(2)	O(5)-B(4)-O(6)	115.9(3)
O(2)-B(1)-C(1)	121.9(3)	O(5)-B(4)-C(4)	120.6(2)
O(3)-B(2)-O(1)	119.3(2)	O(6)-B(4)-C(4)	123.5(2)
O(3)-B(2)-C(2)	122.2(3)		

Symmetry transformations used to generate equivalent atoms:

#1 x, 1/2-y, 1/2+z #2 x, 1/2-y, -1/2+z

Table S6 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $Rb_2(CH_3)_4B_4O_5·4H_2O$, $[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$ and $Li(CH_3)_4B_4O_3(OH)_3$.

Atoms	*x*	*y*	*z*	$U_{(eq)}$
		$Rb_2(CH_3)_4B_4O_5·4H_2O$		
H(1A)	795.38	7217.37	6590.32	110(30)
H(1B)	-145.62	6177.17	6366.12	70(20)
H(1C)	2962.38	9411.59	6203.75	74(18)
H(1D)	2945.48	7681.59	6237.95	55(14)
H(1E)	4202.38	8751.59	6661.95	75(19)
H(2A)	1140.66	5568.28	5343.61	110(30)
H(2B)	1875.66	5339.28	4737.51	100(20)
H(2C)	-1028.87	9339.1	7493.57	35(12)
H(2D)	-1040.97	7555.1	7739.47	77(18)
H(2E)	-819.87	8792.1	8475.47	49(13)
H(3A)	4607.78	5461.38	9157.52	110(20)
H(3B)	3463.78	4890.38	8821.52	150(30)
H(3C)	3747.78	5719.38	9682.52	150(30)
H(4A)	2899.76	12458.23	8844.21	91
H(4B)	4371.66	11891.66	8939.84	91
H(4C)	3608.75	11485.12	9585.2	91
H(8A)	4525.8	2359.21	6829.05	68(18)
H(8B)	3592.1	1267.21	6944.95	90(20)
		$[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$		
H(5)	19587	6965	-3726	107
H(1D)	17183	9719	4994	66
H(1E)	16071	10486	3950	66
H(2D)	17064	9642	962	64
H(2E)	15999	10436	1519	64
H(3D)	18991	8545	4150	71
H(2A)	13994	6894	-6447	82

H(2B)	13994	8106	-6447	82
H(2C)	12609	7500	-5791	82
H(3A)	18871	9495	-853	85(13)
H(3B)	17312	10117	-2149	81(12)
H(3C)	18912	9514	-2515	71(11)
H(1A)	13833	8106	743	89
H(1B)	13833	6894	743	89
H(1C)	12505	7500	-552	89
H(3E)	18790(50)	8430(30)	2520(40)	69(11)
H(4A)	18588	7500	645	79
H(4B)	20194	7500	582	79
H(5)	19587	6965	-3726	107
H(1D)	17183	9719	4994	66
		$Li(CH_3)_4B_4O_3(OH)_3$		
H(4)	9480(20)	3576(12)	1570(30)	50
H(3A)	8239	4709	633	77
H(3B)	8157	4822	2320	77
H(3C)	6272	4968	1313	77
H(4A)	8626	4351	6911	81
H(4B)	6464	4339	7478	81
H(4C)	6807	4278	5805	81
H(1A)	2768	3533	-1834	84
H(1B)	860	3587	-921	84
H(1C)	2018	2872	-992	84
H(2A)	2340	3374	4878	97
H(2B)	1110	4008	4226	97
H(2C)	3107	4147	5110	97
H(6)	6610(60)	3240(20)	8870(50)	75(12)
H(5)	8140(60)	2500(30)	6070(50)	80(13)

Table S7 Hydrogen bonds for $Rb_2(CH_3)_4B_4O_5·4H_2O$, $[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$ and $Li(CH_3)_4B_4O_3(OH)_3$.

D-H ⋯A	d(D-H) (Å)	d(H ⋯A) (Å)	d(D-A) (Å)	D-H-A (°)
$Rb_2(CH_3)_4B_4O_5·4H_2O$				
O(1)-H(1A) ⋯O(3)	0.90	1.78	2.680(4)	172.1
O(2)-H(2A) ⋯O(1)	0.91	2.05	2.848(5)	146.2
O(2)-H(2B) ⋯O(4)#4	0.97	1.96	2.858(5)	152.4
O(8)-H(8A) ⋯O(5)#1	0.89	1.87	2.759(4)	175.1
O(9)-H(9A) ⋯O(3)#2	0.88	1.90	2.776(4)	172.0
O(9)-H(9B) ⋯O(7)#3	0.91	1.94	2.851(4)	171.8
Symmetry transformations used to generate equivalent atoms:				
#1 1-x, -1/2+y, 3/2-z	#2 x, 5/2-y, 1/2+z	#3 -x, 2-y, 2-z	#4 x, 3/2-y, -1/2+z	
$[C(NH_2)_3]_2(CH_3)_4B_4O_5·2H_2O$				
N(1)-H(1E) ⋯O(1)#1	0.86	2.01	2.859(3)	172.2
N(2)-H(2E) ⋯O(2)#1	0.86	1.99	2.846(3)	176.5
Symmetry transformations used to generate equivalent atoms:				
#1 3-x, 2-y, -z				
$Li(CH_3)_4B_4O_3(OH)_3$				
O(4)-H(4) ⋯O(1)#1	0.873(9)	2.062(13)	2.868(2)	153.2(19)
O(6)-H(6) ⋯O(2)#2	0.88(4)	1.77(4)	2.642(3)	168(4)
O(5)-H(5) ⋯O(4)#3	0.88(5)	1.79(5)	2.663(3)	175(4)
Symmetry transformations used to generate equivalent atoms:				
#1 1+x, y, z	#2 x, y, 1+z	#3 x, 1/2-y, 1/2+z		

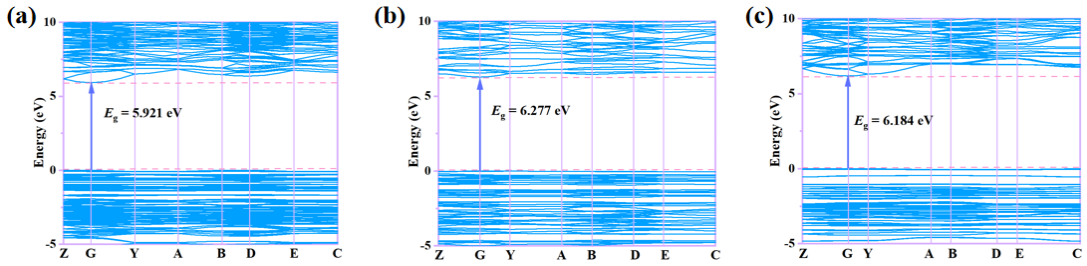

Fig. S1 Band structure of (a) RCHBO, (b) GCHBO and (c) LCHBO.

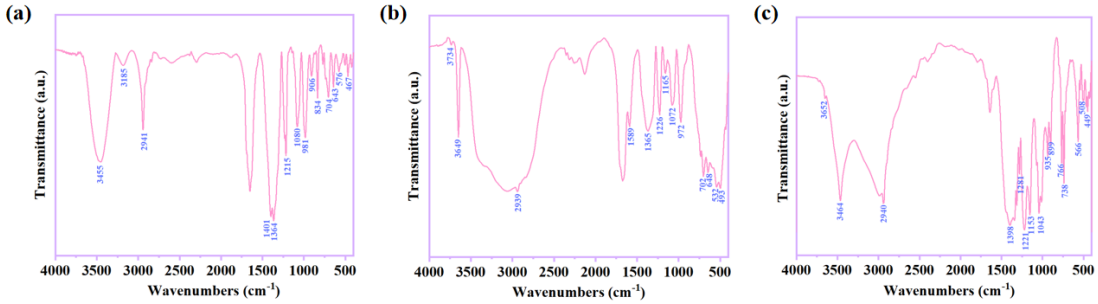

Fig. S2 Infrared spectra of (a) RCHBO, (b) GCHBO and (c) LCHBO.

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