

Electronic Supplementary Information

The Study on The Different Mechanoluminescence of Anthracene Derivatives

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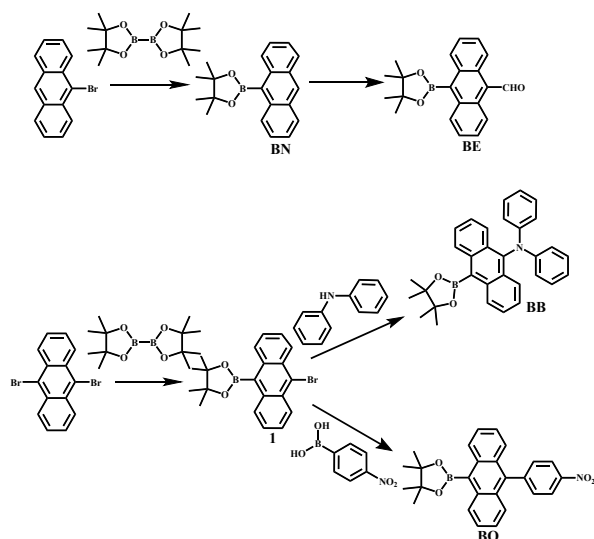
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1. Experimental Section

Instruments and methods: ^1H and ^{13}C spectra were recorded on a 500MHz Bruker AVANCZ III spectrometer, DMSO were selected as the solvent with tetramethylsilane (TMS) as the internal standard ($\delta = 0.00$ ppm). A Thermo Fisher ITQ1100 GC-MS mass detector was used to record the mass spectra. UV-vis absorption spectra was performed on UV-2550 spectrophotometer and photoluminescence spectra were recorded RF-5301PC spectrofluorophotometer. Fluorescence decay was measured on an Edinburgh FLS980 fluorescence spectrophotometer and absolute photoluminescence quantum yield (PLQY) was measured on an Edinburgh FLS920 fluorescence spectrophotometer. The PXRD (powder X-ray diffraction) patterns were recorded on a Rigaku SmartLab (3) diffractometer at a scan rate of $5^\circ/\text{min}$. The ML spectra were measured on Ocean Optics spectrometer as a power detector. The single-crystal X-ray diffraction data were recorded by a R-Axis RAPID diffractometer. The ground state (S_0) geometry was obtained from the single crystal structure and no further geometry optimization was conducted in order to maintain the specific molecular configuration and corresponding intermolecular locations. DSC measurements were carried out on a NETZSCH DSC 200F3 instrument at a heating rate and a cooling rate of $10^\circ\text{C min}^{-1}$ in nitrogen.

2. Synthesis



Scheme S1. The synthetic route of BN, BO, BE and BB.

Synthesis of 2-(anthracen-9-yl)-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane

(BN):

a mixture of 9-bromoanthracene (257.1 mg, 1 mmol), bis(pinacolato)diboron (380.9 mg, 1.5 mmol), Pd(dppf)Cl₂ (24.5 mg, 0.03 mmol) and potassium acetate (588.8 mg, 6 mmol) were dissolved in 10 mL of 1,4-dioxane. The solution was heated with stirring at 80 °C for 24 h under nitrogen. The cooled mixture was washed with water and extracted with methylene chloride (DCM). Then the DCM solution was dried with anhydrous magnesium sulfate overnight. After removing the solvent, the obtained crude product was purified by silica gel chromatography using DCM/petroleum ether (1:4, v/v) as elute, to obtained white solid of BN. The yield was 80.3%, 246.5 mg. ¹H NMR (500 MHz, DMSO) δ 8.68 (s, 1H), 8.31 (d, J = 8.6 Hz, 2H), 8.11 (d, J = 7.9 Hz, 2H), 7.59 – 7.50 (m, 4H), 1.53 (s, 12H). MS (ESI), m/z: 303.89, calcd for C₂₀H₂₁BO₂:304.20.

Synthesis of 10-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) anthracene -9-

carbaldehyde (BE):

Under the protection of nitrogen, the BN (304.2 mg, 1 mmol) obtained above was added into anhydrous tetrahydrofuran (10ml). Then, adding n-butyllithium (2.5M, 0.5 ml) under -70 °C. Stirring for one hour, adding dimethyl formamide (80.4 mg, 1.1 mmol) to solution slowly. After addition, keep stirring at this temperature for one hour, and then naturally rise to room temperature and stir for three hours. After the test reaction was completed, deionized water was added to quench the reaction. The cooled mixture was extracted with DCM. Then the DCM solution was dried with anhydrous magnesium sulfate overnight. After removing the solvent, the obtained crude product was purified by silica gel chromatography using DCM/petroleum ether (1:1, v/v) as elute, to obtained yellow solid of BE. The yield was 83.3%. ¹H NMR (500 MHz, DMSO) δ 11.49 (s, 1H), 8.95 (s, 2H), 8.25 (d, J = 8.5 Hz, 2H), 7.75 (s, 2H), 7.68 (s, 2H), 1.56 (s, 12H). MS (ESI), m/z: 331.59, calcd for C₂₁H₂₁BO₃:332.21.

Synthesis of 2-(10-bromoanthracen-9-yl)-4, 4, 5, 5 -tetramethyl-1, 3, 2 – dioxaborolane (1):

A mixture of 9, 10-dibromoanthracene (336.2 mg, 1 mmol), bis(pinacolato)diboron (380.9 mg, 1.5 mmol), Pd(dppf)Cl₂ (24.5 mg, 0.03 mmol) and potassium acetate (588.8 mg, 6 mmol) were dissolved in 10 mL of 1,4-dioxane. The solution was heated with stirring at 80 °C for 24 h under nitrogen. The cooled mixture was washed with water and extracted with DCM. Then the DCM solution was dried with anhydrous magnesium sulfate overnight. After removing the solvent, the obtained crude product was purified by silica gel chromatography using DCM/petroleum ether (1:4, v/v) as elute, to obtained light green solid of 1. The yield was 85.3%, 325.5 mg. ¹H NMR (500 MHz, DMSO) δ 8.50 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 8.6 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.70 – 7.63 (m, 2H), 1.54 (s, 12H). MS (ESI), m/z: 383.85, calcd for C₂₀H₂₀BBrO₂:383.07.

Synthesis of N, N-diphenyl-10-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) anthracen-9-amine (BB):

In a nitrogen atmosphere, diphenylamine (169.2 mg, 1.2 mmol), compound 1 (383.2 mg, 1 mmol), Pd₂(dba)₃ (27 mg, 0.03 mmol), *t*-Bu₃P (8 mg, 0.09 mmol) and *t*-BuOK (108 mg, 1 mmol) were dissolved in 15 ml of toluene, and then stirred at a temperature of 85 °C for 4 hours. The reaction solution was cooled to room temperature, and then extraction was performed with water and DCM. The organic extracts were dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The obtained product was purified by silica gel chromatography using DCM as elute, to obtain yellow solid of BB. The yield was 61.5%. ¹H NMR (500 MHz, DMSO) δ 8.37 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.52 – 7.47 (m, 2H), 7.19 (t, J = 7.9 Hz, 4H), 6.97 – 6.87 (m, 6H), 1.55 (s, 12H). MS (ESI), m/z: 470.43, calcd for C₃₂H₃₀BNO₂:471.41.

Synthesis of 4, 4, 5, 5-tetramethyl-2-(10-(4-nitrophenyl) anthracen-9-yl) - 1, 3, 2-dioxaborolane (BO):

A mixture of compound 1 (383.2 mg, 1 mmol), (4-nitrophenyl)boronic acid (167.0 mg, 1 mmol), and Pd(PPh₃)₄ (0.03 mmol, 34.5 mg) were added into a 50 mL flask. Potassium carbonate (1.1 mmol, 0.7 g) was dissolved in 4 mL water and then the solution was added to the 50 mL flask. Toluene (12 mL) and ethyl alcohol (5 mL) were added to the above flask, and the solution was refluxed at 85 °C for 48 h under nitrogen. The cooled mixture was quenched with dilute hydrochloric acid solution and extracted with DCM. The organic extracts were dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The obtained product was purified by silica gel chromatography using DCM as elute, to obtain yellow solid of BO. The yield was 64.5%. ¹H NMR (500 MHz, DMSO) δ 8.49 (d, J = 8.5 Hz, 2H), 8.34 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.59 (dd, J = 8.5, 4.0 Hz, 2H), 7.47 (d, J = 3.4 Hz, 4H), 1.56 (s, 12H). MS (ESI), m/z: 424.86, calcd for C₂₆H₂₄BNO₄:425.29.

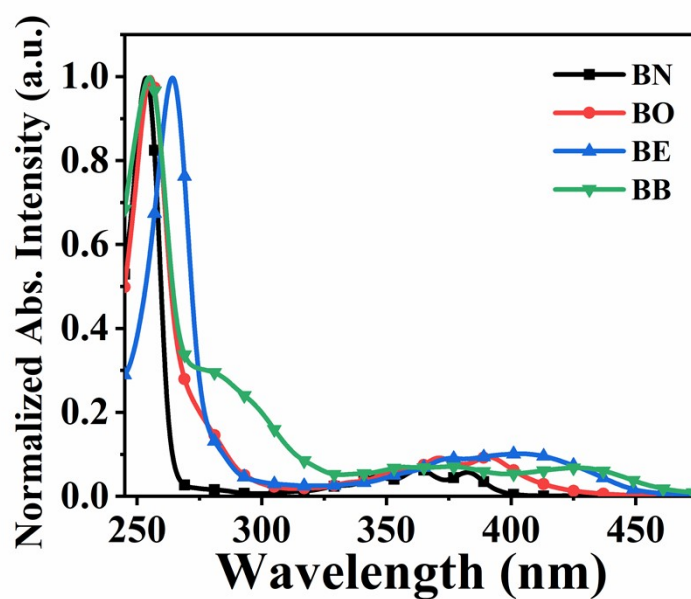


Fig. S1 UV-visible absorption spectra of BN, BO, BE and BB in THF solutions (10^{-5} M).

Table. S1 Optical properties of BN, BO, BE and BB

Compound	$\lambda_{em}(nm)$	ΦF (%)	τ (ns)	K_r ($10^8 s^{-1}$)	K_{nr} ($10^8 s^{-1}$)
BN(Solution)a	425	36.77	7.23	0.509	0.875
BN(Powder)	431	33.03	8.42	0.392	0.795
BO(Solution) a	545	9.48	3.19	0.297	2.84
BO (Powder)	500	2.54	1.73	0.147	5.64
BE(Solution) a	430	0.09	3.81	0.00236	2.62
BE(Powder)	545	5.16	16.2	0.0318	0.584
BB(Solution) a	510	55.76	17.3	0.322	0.255
BB(Powder)	495	36.34	12.9	0.282	0.494

a: Measured in a dilute THF solution, 10^{-5} M;

The radiative rate (K_r) can be obtained using equation $K_r = \Phi F / \tau$;

The non-radiative rate (K_{nr}) can be estimated from the equation $\Phi F = K_r / (K_r + K_{nr})$

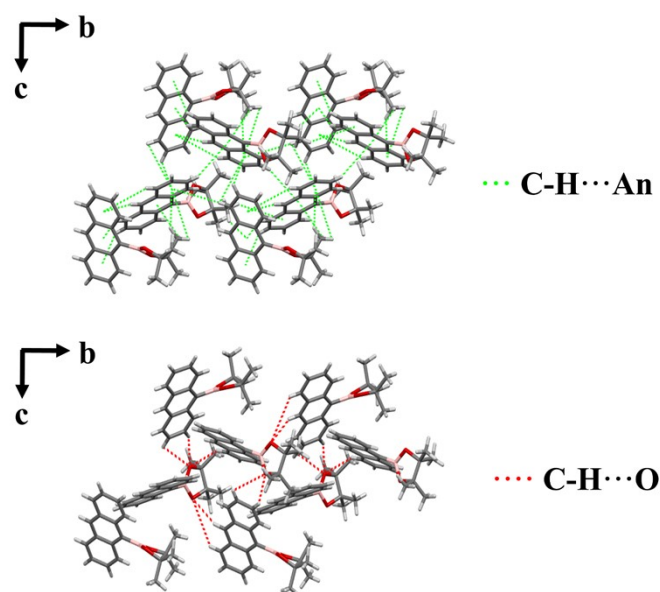


Fig. S2 The intermolecular interactions including C-H... π (green) and C-H...O (red lines) in BN crystal (eight molecules).

Table. S2 Summarization of the C-H... π , C-H...O intermolecular interactions in BN crystal.

Molecule	Orientation of Interaction	d /Å	Number	
BN	1	C-H...An	3.932	4
	2	C-H...An	2.859	4
	3	C-H...An	3.063	4
	4	C-H...An	3.793	4
	5	C-H...An	3.993	4
	6	C-H...An	2.993	4
	7	C-H...An	3.293	4
	8	C-H...An	3.159	3
	9	C-H...An	3.844	3
	10	C-H...An	3.638	3
	11	C-H...An	3.931	2
	12	C-H...An	3.822	2
	13	C-H...An	3.681	2
	1	C-H...O	3.502	3
	2	C-H...O	2.611	3
	3	C-H...O	3.978	2
	4	C-H...O	3.811	2
	5	C-H...O	3.795	2

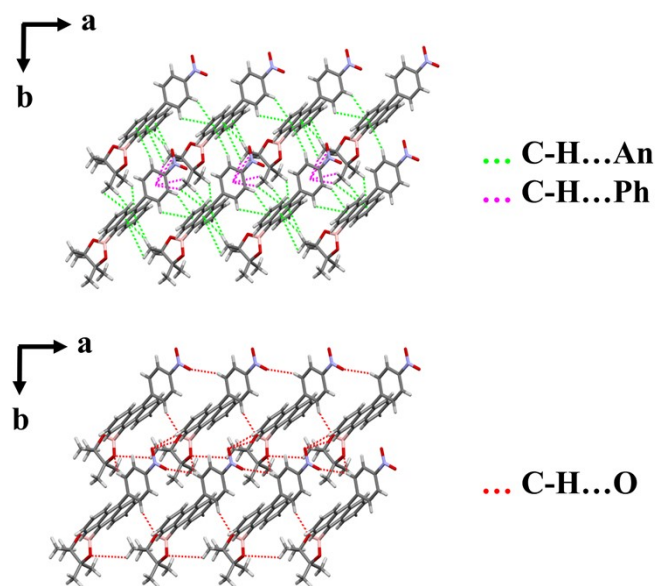


Fig. S3 The intermolecular interactions including C-H $\cdots\pi$ (green /violet lines), C-H \cdots O (red lines) in BO crystal (eight molecules).

Table. S3 Summarization of the C-H $\cdots\pi$, C-H \cdots O intermolecular interactions in BO crystal.

Molecule	Orientation of Interaction	d /Å	Number	
BO	1	C-H \cdots An	2.761	6
	2	C-H \cdots An	2.620	6
	3	C-H \cdots An	3.854	6
	4	C-H \cdots An	2.887	6
	5	C-H \cdots An	3.770	6
	6	C-H \cdots An	3.311	4
	7	C-H \cdots An	3.489	4
	8	C-H \cdots An	2.603	4
	9	C-H \cdots An	3.872	4
	10	C-H \cdots Ph	3.985	3
	11	C-H \cdots Ph	3.282	3
	12	C-H \cdots Ph	3.540	3
	13	C-H \cdots Ph	3.881	3
	1	C-H \cdots O	2.720	6
	2	C-H \cdots O	3.048	6
	3	C-H \cdots O	3.850	6
	4	C-H \cdots O	3.504	4
	5	C-H \cdots O	2.683	3
	6	C-H \cdots O	2.939	3

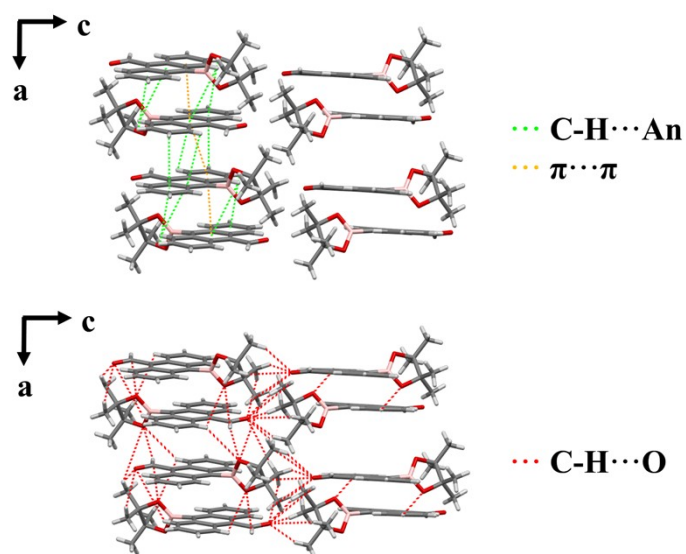


Fig. S4 The intermolecular interactions including C-H... π (green), π ... π (orange), C-H...O (red lines) in BE crystal (eight molecules).

Table. S4 Summarization of the C-H... π , π ... π , C-H...O intermolecular interactions in BE crystal.

Molecule	Orientation of Interaction	d /Å	Number	
BE	1	C-H...An	3.499	4
	2	C-H...An	3.804	4
	3	C-H...An	3.385	2
	4	C-H...An	3.730	2
	1	π ... π	3.665	1
	2	π ... π	3.656	2
	1	C-H...O	2.927	4
	2	C-H...O	2.845	4
	3	C-H...O	2.958	4
	4	C-H...O	3.060	4
	5	C-H...O	2.635	4
	6	C-H...O	3.938	4
	7	C-H...O	3.034	4
	8	C-H...O	3.942	4
	9	C-H...O	2.785	4
	10	C-H...O	3.966	2
	11	C-H...O	3.941	2
	12	C-H...O	2.551	2
	13	C-H...O	3.118	2
	14	C-H...O	3.180	1
	15	C-H...O	3.299	1

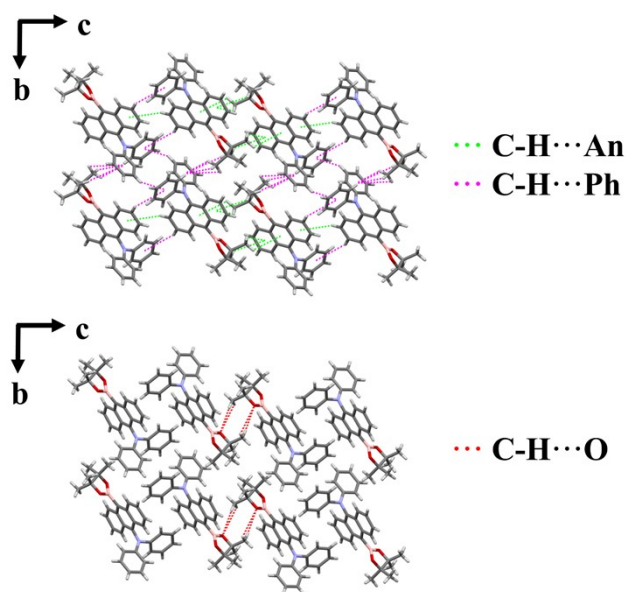


Fig. S5 The intermolecular interactions including C-H··· π (green /violet lines), C-H···O (red lines) in BB crystal (eight molecules).

Table. S5 Summarization of the C-H... π , C-H···O intermolecular interactions in BB crystal.

Molecule	Orientation of Interaction	d /Å	Number	
BB	1	C-H···An	3.853	4
	2	C-H···An	3.221	4
	3	C-H···An	3.461	4
	4	C-H···An	3.426	4
	1	C-H···Ph	3.911	4
	2	C-H···Ph	3.459	4
	3	C-H···Ph	3.814	4
	4	C-H···Ph	2.951	4
	5	C-H···Ph	3.640	4
	6	C-H···Ph	3.878	4
	1	C-H···O	3.193	4
	2	C-H···O	3.294	4

Table. S6 The Crystal data of BN, BO, BE and BB.

Compound	Crystal system	Space group	Symmetry	ML property
BN	monoclinic	P2 ₁	Non-Centrosymmetric	Active
BO	triclinic	P1	Non-Centrosymmetric	Weak-Active
BE	monoclinic	P2 ₁ /c	Centrosymmetric	Inactive
BB	triclinic	P-1	Centrosymmetric	Inactive

Table. S7 Structural data crystal of BN, BO, BE and BB.

Name	BN	BO	BE	BB
Empirical formula	C ₂₀ H ₂₁ BO ₂	C ₂₆ H ₂₄ BNO ₄	C ₂₁ H ₂₁ BO ₃	C ₃₂ H ₃₀ BNO ₂
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	P2 ₁	P1	P2 ₁ /c	P-1
Unit cell Angles (°)	α=90	α=96.665(3)	α=90	α=93.642(3)
	β=109.928(2)	β=110.884(3)	β=96.3500(10)	β=99.389(3)
	γ=90	γ=101.244(3)	γ=90	γ=103.657(3)
Unit cell lengths (Å)	a=10.6429(5)	a=7.4244(5)	a=7.1705(3)	a= 7.3775(5)
	b=11.1771(5)	b=8.6004(6)	b=10.3149(5)	b= 10.9532(9)
	c=15.0198(7)	c=9.7179(7)	c=23.0801(10)	c=16.1075(12)
Unit cell volume (Å ³)	1679.72(14)	556.84(7)	1696.60(13)	1240.77(16)
Z	4	1	4	2
Density (g/cm ³)	1.203	1.268	1.301	1.262
F (000)	648.0	224.0	704.0.	500.0
CCDC number	2048014	2048016	2048015	2089171

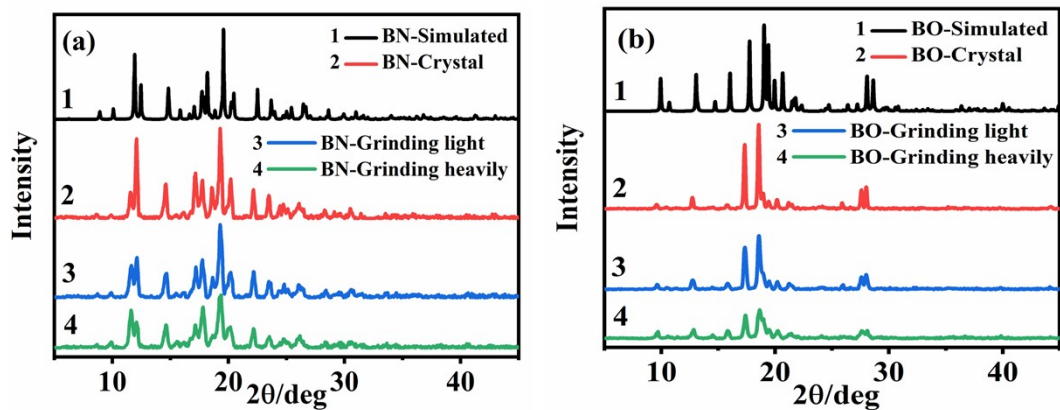
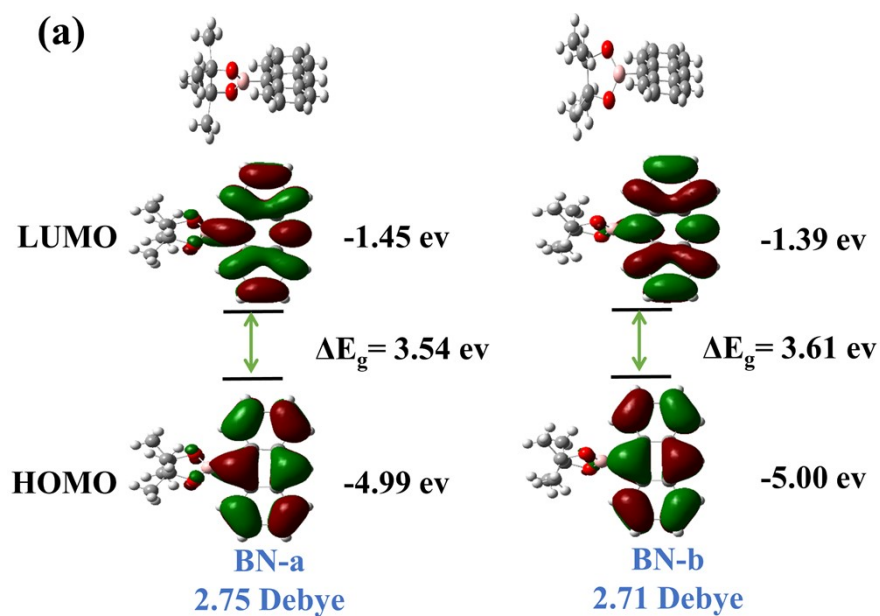


Fig. S6 The PXR D patterns of BN (a) and BO (b) in the crystalline state, after light grinding and heavy grinding, respectively.



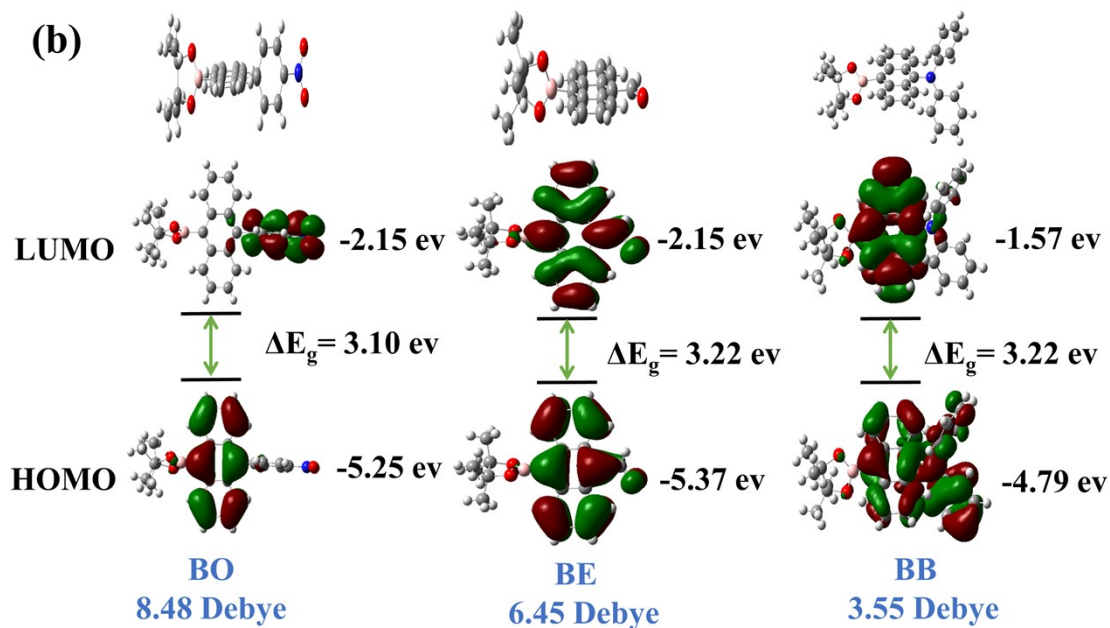


Fig. S7 The HOMO-LUMO levels, energy gaps and dipole moments of isolated molecules in BN(a), BO BE and BB(b). (Calculated at the B3LYP/6-31G (d, p) level).

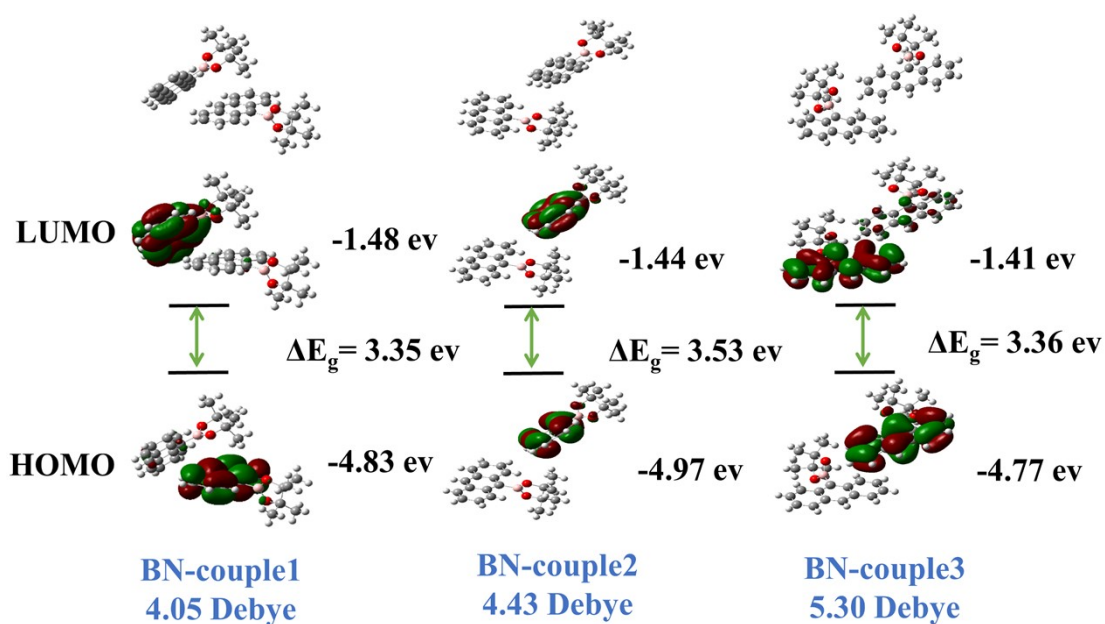


Fig. S8 The HOMO-LUMO levels, energy gaps and dipole moments of coupled moleculars in BN crystal calculated at the B3LYP/6-31g (d, p) level.

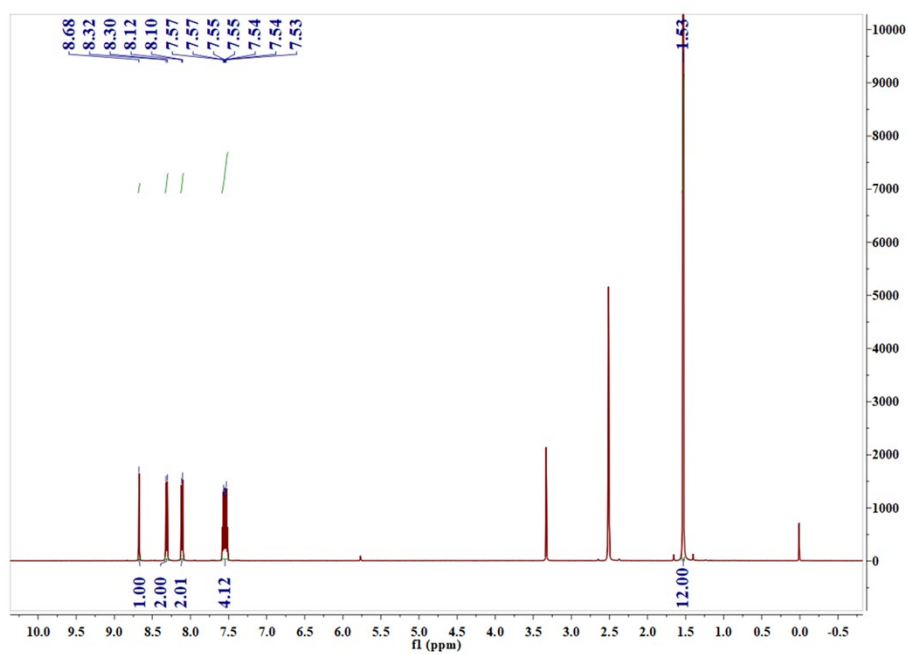


Fig. S9 ^1H NMR spectrum of BN conducted in DMSO.

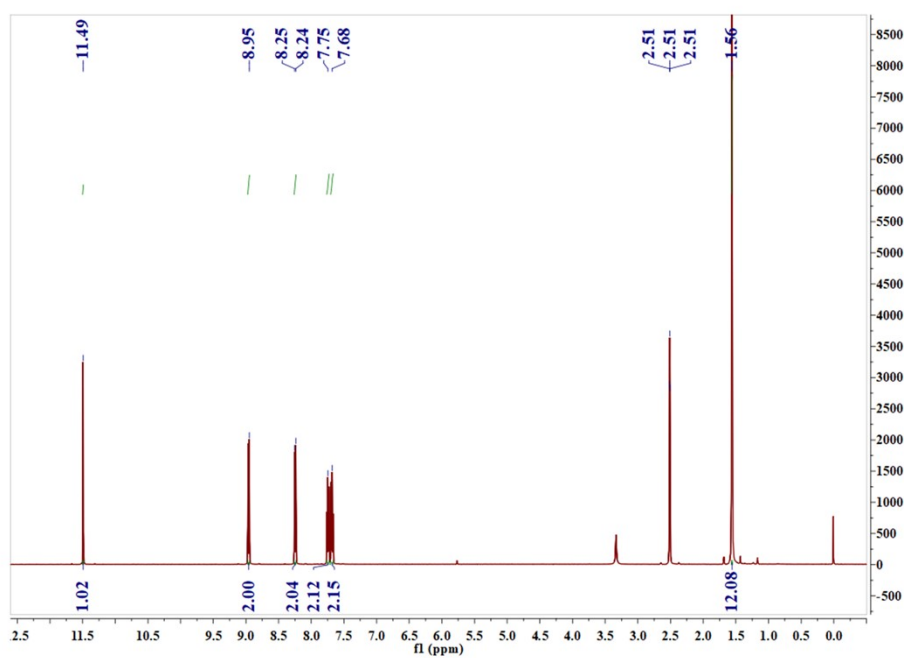


Fig. S10 ^1H NMR spectrum of BE conducted in DMSO.

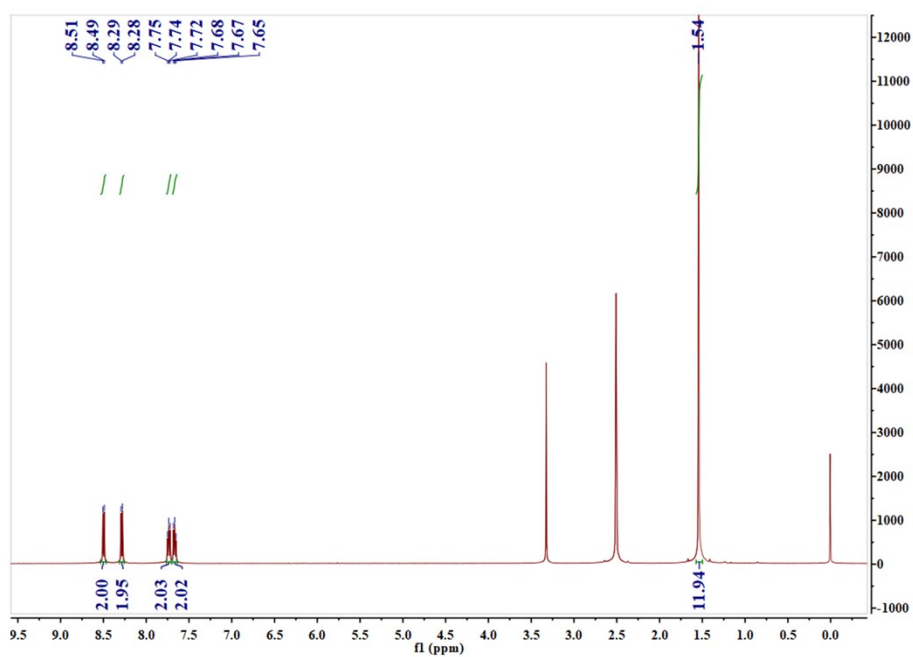


Fig. S11 ^1H NMR spectrum of 1 conducted in DMSO.

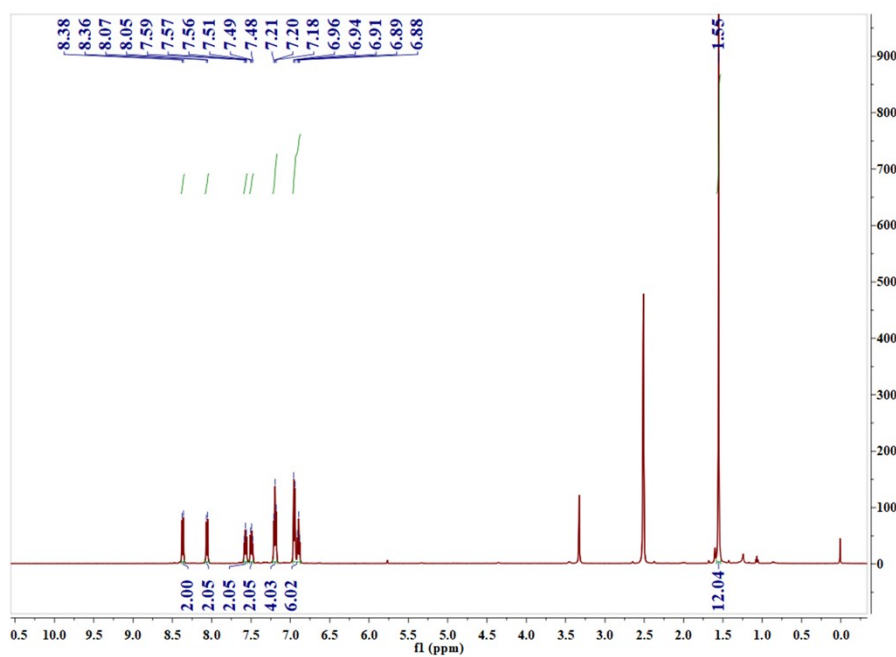


Fig. S12 ^1H NMR spectrum of BB conducted in DMSO.

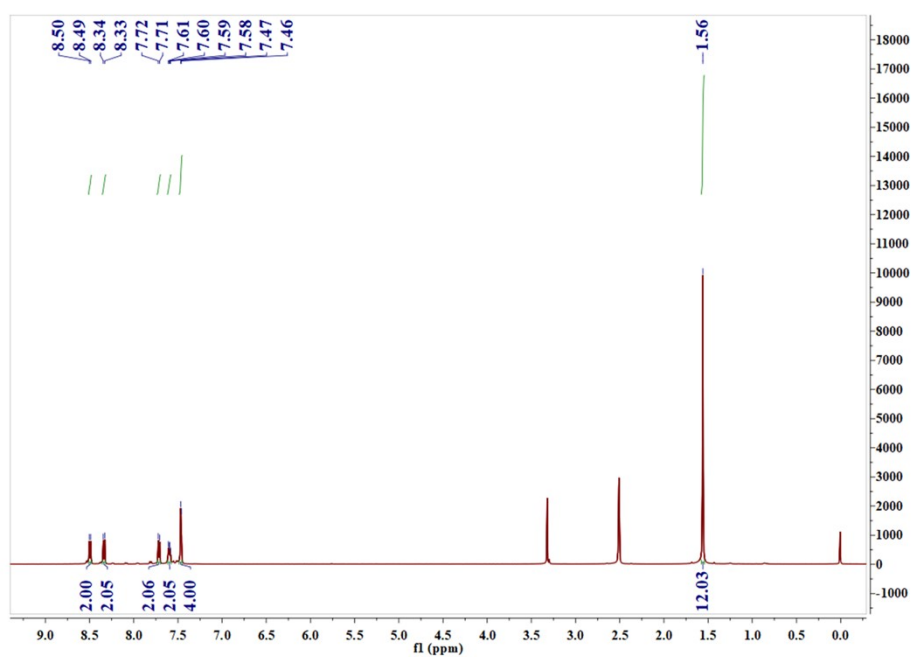


Fig. S13 ^1H NMR spectrum of BO conducted in DMSO.

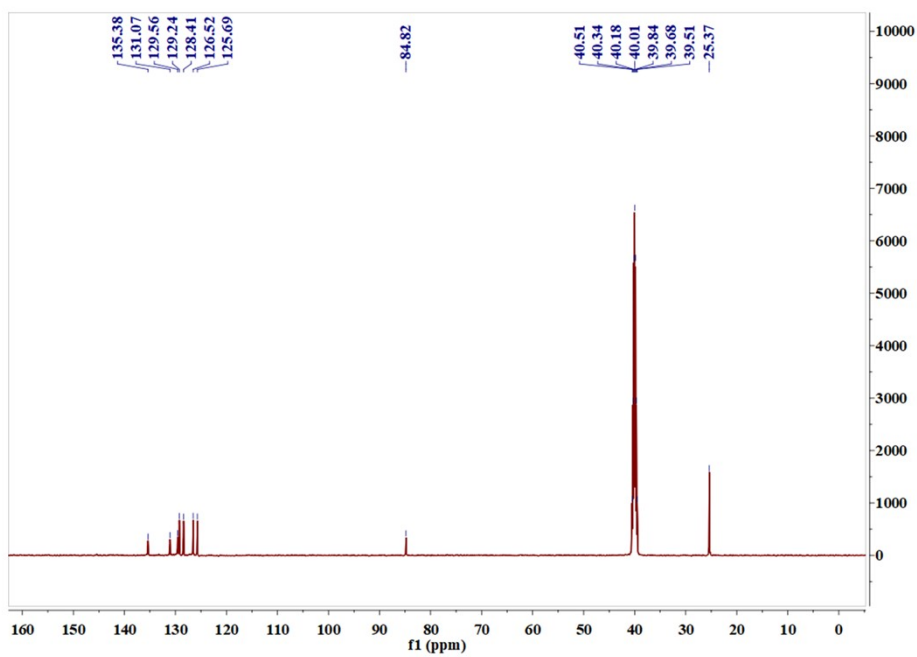


Fig. S14 ^{13}C NMR spectrum of BN conducted in DMSO.

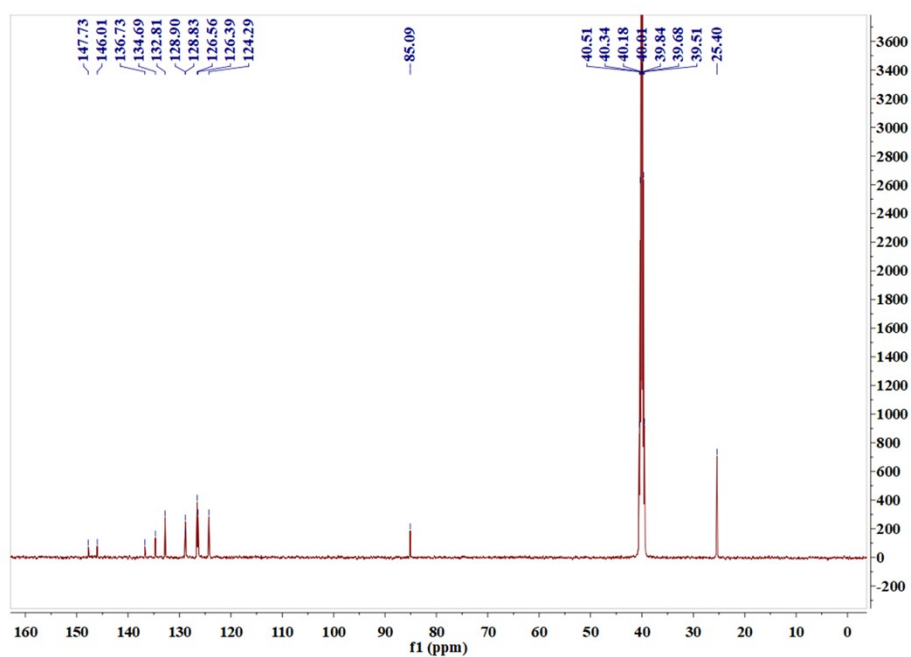


Fig. S15 ^{13}C NMR spectrum of BO conducted in DMSO.

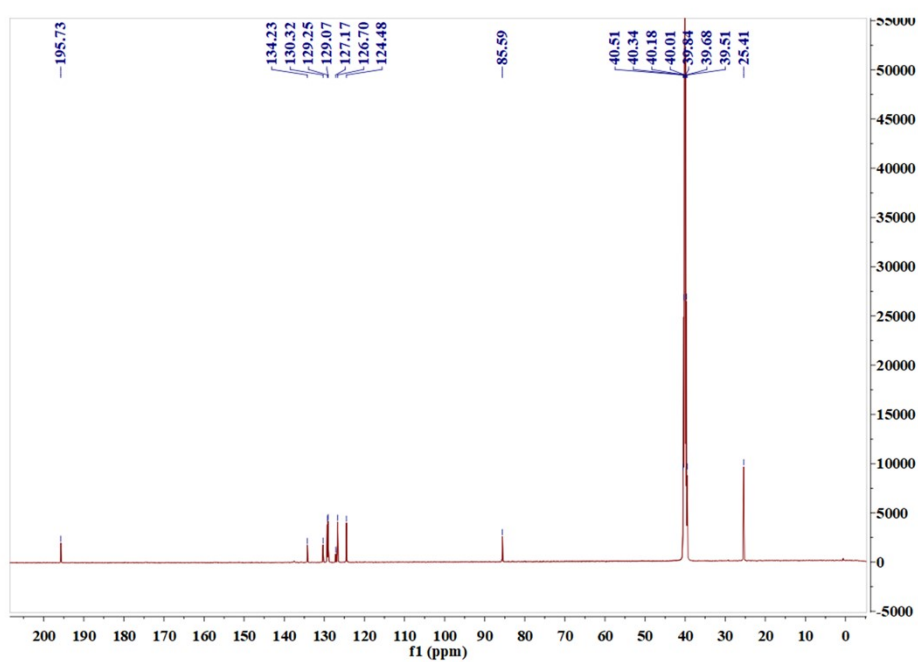


Fig. S16 ^{13}C NMR spectrum of BE conducted in DMSO.

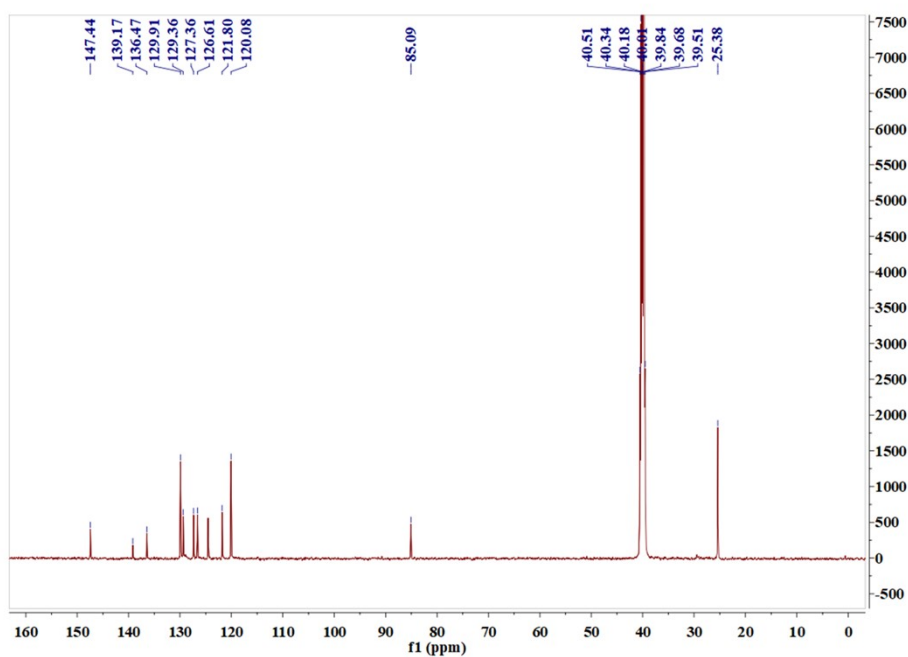


Fig. S17 ^{13}C NMR spectrum of BB conducted in DMSO.

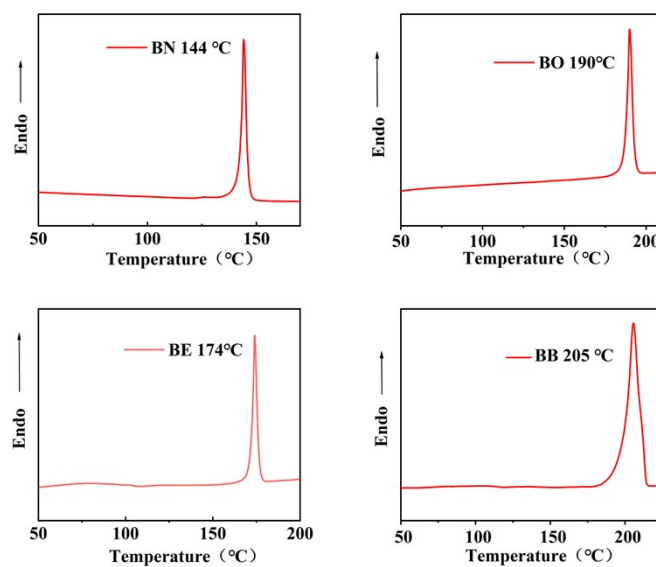


Fig. S18 DSC curves of the BN, BO, BE and BB.