Supporting Information (SI)

Planar [5,5] Fused-ring Framework in Perovskite Energetic Materials: A One-pot Assembly Toward High-Energy-Density Materials

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1. General Methods

^{1}H and ^{13}C NMR spectra were recorded on 300 MHz (Bruker AVANCE 300) clear magnetic resonance spectrometers operating at 300 and 75 MHz, respectively, by using DMSO-d_6 as the solvent and locking solvent. The DSC test was performed on the SDT-Q600 instrument at a heating rate of 10 °C min^{-1} under a nitrogen flow of 50 mL min^{-1} in a closed aluminum crucible. Detonation velocity and pressure were calculated using the K–J equations. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 °C， using KBr plates to prepare thin films. Elemental analyses were performed using the Vario Micro cube Elementar Analyzer. Impact and friction sensitivities were assessed with a standard BAM Fall Hammer and BAM Friction Tester, respectively. Densities were determined at 25 °C with a Micromeritics AccuPyc II 1340 gas pycnometer.

The data were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173(2) K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

2. The Experiment and Crystallographic Data

Caution！

Some of the compounds involved in this experiment are dangerous, so it is necessary to strictly follow laboratory safety regulations during the experiment and to wear face shields and leather gloves as required.

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^{1}H and ^{13}C spectra are recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300 and 75 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of 5°C min^{-1}. IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by

using KBr plates. Densities are determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by K–J equations.

Common synthesis of BPP.

2,4,5,6-tetrahydropyrrolo[3,4-c]pyrazole (0.22 g, 2.00 mmol) was dissolved in 2 mL of water, then ammonium perchlorate (0.23 g, 2.00 mmol) and 0.60 mL of perchloric acid (70%) solution were added. The reaction was carried out at 60 ℃ for 30 min, cooled to room temperature, filtered, and the filter residue was washed with ethanol three times, followed by vacuum drying to obtain a white solid. Yield: 0.79 g, 92.4%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.58 (s, 2H), 7.60 (s, 1H), 7.18 (s, 4H), 4.27 (t, 4H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ =152.60, 123.66, 117.53 44.49, 43.73 ppm. IR (KBr): 3236, 1573, 1479, 1421, 1251, 1029, 955, 927, 881, 665, 618, 467, 430 cm^{-1}. Elemental analysis for $C_5H_{13}Cl_3N_4O_{12}$ (427.54): calcd. C 14.05, H 3.07, N 13.11 %, found: C 13.88, H 2.91, N 13.18 %

X-ray Crystallography

The crystal of **BPP** were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å), respectively. Integration and scaling of intensity data were accomplished using the SAINT program2. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full- matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS4 Relevant crystal data and refinement results are summarized in **Table S1.**

Table S1. Crystal data and structure refinement for **BPP**

Crystal	**BPP**
Empirical formula	$C_5H_{13}Cl_3N_4O_{12}$
Formula weight	427.54
CCDC	2536776
Crystal system	monoclinic
Temperature/K	193K
a/ Å	10.6789(3)
b/ Å	16.0290(5)

c/ Å	8.7377(3)
α/ °	90
β/ °	95.7440(10)
γ/ °	90
Volume/Å^3	1488.14(8)
Formula Z	4
Density (g cm^{-3})	1.908
Space group	$P2_1/c$
μ (mm^{-1})	0.690
F (000)	872.0
Radiation	MoKα (λ = 0.71073)
Crystal size (mm3)	0.15 × 0.12 × 0.1
2Θ range for data collection/°	4.6 to 54.988
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -11 ≤ l ≤ 11
Reflections collected	37718
Independent reflections	3401 [R_{int} = 0.0714, R_{sigma} = 0.0286]
Data/restraints/parameters	3401/6/228
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0912
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0964
Largest diff. peak/hole / e Å^{-3}	0.41/-0.50

Table S2. Bond distance of **BPP**

Parameter	**Å**	**Parameter**	**Å**
Cl1-O1	1.4293(18)	N2-H2A	0.91
Cl1-O2	1.4350(16)	N2-H2B	0.91
Cl1-O3	1.4529(15)	N3-H3	0.88
Cl1-O4	1.4419(16)	N4-H4	0.88
Cl2-O6	1.4496(16)	N1-H1A	0.87
Cl2-O7	1.4359(18)	N1-H1C	0.85(4)
Cl2-O5	1.4381(17)	N1-H1B	0.87
Cl2-O8	1.4279(17)	N1-H1D	0.86(4)
Cl3-O9	1.4086(19)	C1-C2	1.365(3)
Cl3-O10	1.4369(17)	C2-C4	1.370(3)
Cl3-O12	1.4444(18)	C2-C3	1.487(3)

Cl3-O11	1.4367(18)	C4-C5	1.476(3)
N2-C5	1.519(3)	C1-H1	0.95
N2-C3	1.526(2)	C3-H3A	0.99
N3-N4	1.347(2)	C3-H3B	0.99
N3-C4	1.335(3)	C5-H5A	0.99
N4-C1	1.343(3)	C5-H5B	0.99

Table S3. Bond angle of **BPP**

Parameter	°	**Parameter**	°
O3-Cl1-O4	108.77(9)	N3-N4-H4	125
O1-Cl1-O4	109.65(10)	C1-N4-H4	125
O1-Cl1-O2	110.79(10)	H1A-N1-H1D	104
O1-Cl1-O3	109.16(10)	H1B-N1-H1C	114
O2-Cl1-O3	108.44(9)	H1C-N1-H1D	115(4)
O2-Cl1-O4	109.99(9)	H1A-N1-H1B	105
O5-Cl2-O6	108.17(10)	H1B-N1-H1D	111
O5-Cl2-O8	109.81(10)	H1A-N1-H1C	107
O6-Cl2-O7	108.80(10)	N4-C1-C2	106.71(16)
O5-Cl2-O7	109.04(10)	C3-C2-C4	112.19(16)
O7-Cl2-O8	110.72(10)	C1-C2-C4	107.08(17)
O6-Cl2-O8	110.25(10)	C1-C2-C3	140.73(17)
O9-Cl3-O12	110.93(13)	N2-C3-C2	100.96(15)
O9-Cl3-O11	110.64(12)	C2-C4-C5	113.87(17)
O9-Cl3-O10	110.88(12)	N3-C4-C2	109.09(16)
O10-Cl3-O12	108.33(11)	N3-C4-C5	137.03(18)
O11-Cl3-O12	107.05(11)	N2-C5-C4	100.68(14)
O10-Cl3-O11	108.89(11)	N4-C1-H1	127
C3-N2-C5	112.29(15)	C2-C1-H1	127
N4-N3-C4	106.83(17)	N2-C3-H3A	112
N3-N4-C1	110.29(17)	C2 -C3-H3B	112
C3-N2-H2A	109	H3A-C3-H3B	109
C3-N2 -H2B	109	C2-C3-H3A	112
C5-N2-H2A	109	N2-C3-H3B	112
C5-N2-H2B	109	N2-C5-H5B	112
H2A-N2-H2B	108	N2-C5-H5A	112
C4-N3-H3	127	H5A-C5-H5B	109

N4-N3-H3	127	C4-C5-H5A	112
C4-C5-H5B	112		

Table S4. Torsion angle of **BPP**

Parameter	°	**Parameter**	°
C5-N2-C3-C2	-0.3(2)	C1-C2-C3-N2	-179.5(3)
C3-N2-C5-C4	-0.2(2)	C4-C2-C3-N2	0.7(2)
C4-N3-N4-C1	-0.1(2)	C1-C2-C4-N3	-0.2(2)
N4-N3-C4-C2	0.2(2)	C1-C2-C4-C5	179.22(18)
N4-N3-C4-C5	-179.0(2)	C3-C2-C4-N3	179.71(17)
N3-N4-C1-C2	0.0(2)	C3-C2-C4-C5	-0.9(2)
N4-C1-C2-C3	-179.7(2)	N3-C4-C5-N2	179.8(2)
N4-C1-C2-C4	0.1(2)	C2-C4-C5-N2	0.7(2)

Table S5. Hydrogen bonds of **BPP**

D-H···A	**d(D-H)/ Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**∠(DHA)/ °**
N1-H1A···O3	0.87	2.15	2.913(2)	147
N1-H1A···O12	0.87	2.56	3.139(3)	125
N1-H1B···O4	0.87	2.6	3.248(2)	132
N1-H1B···O5	0.87	2.19	2.974(2)	150
N1-H1C···O3	0.85(4)	2.16(4)	2.991(2)	166(4)
N1-H1D···O7	0.86(4)	2.16(4)	2.982(3)	160(4)
N2-H2A···O4	0.91	2.24	3.081(2)	153
N2-H2B···O4	0.91	2.32	3.024(2)	134
N2-H2B···O5	0.91	2.25	2.941(2)	132
N2-H2B···O6	0.91	2.53	3.114(2)	123
N3-H3···O3	0.88	2.47	2.987(2)	118
N3-H3···O10	0.88	2.3	3.010(2)	138
N3-H3···O12	0.88	2.51	3.171(3)	133
N4-H4···O12	0.88	2.11	2.929(3)	155
N4-H4···O10	0.88	2.55	3.009(3)	113
C1-H1···O1	0.95	2.24	3.131(3)	155
C3-H3A···O2	0.99	2.51	3.320(3)	139
C3-H3A···O7	0.99	2.55	3.248(3)	128

C3-H3B···O2	0.99	2.6	3.174(2)	117
C3-H3B···O11	0.99	2.46	3.192(3)	130
C5-H5A···O9	0.99	2.55	3.398(3)	144
C5-H5A···O1	0.99	2.42	3.205(3)	135

3. Theoretical Study

Detonation parameters estimated by using DFT calculation and extended K–J equation

For **BPP**, their detonation products can be described as N_2 (g), H_2O (g), CO_2 (g), and C (s). Accordingly, the complete detonation reactions are assumed:

For **BPP**, $[C_5H_9N_3][NH_4](ClO_4)_3 = 2H_2O(g)+2N_2(g)+5CO_2(s)+3HCl(g)+3H_2(g)$

Based on these reactions, the detonation energy (ΔE_{det}) was calculated by DFT method with the code DMoL3 [2] under 3D periodic boundary conditions. The Monkhorst–Pack multiple K-point sampling of the Brillouin zone [3] and the Perdew–Becke–Ezerhoff (PBE) exchange-correlation function were employed in calculation. [4] The results are listed in Table S6. Then the obtained ΔE_{det} was used to estimate the detonation heat (ΔH_{det}; kcal·g^{-1}) from an empirical linear correlation equation [2]:

$$\Delta H_{det} = 1.127\Delta E_{det} + 0.046,\ r = 0.968 \quad (1)$$

where, r represents linear coefficient.

Table S6 Calculated (DMoL3/PBE) total energy (hartree) used in the detonation reactions.

Compound	**BPP**	CO_2	N_2	HCl
Total energy (hartree)	-2698.547	-188.479	-109.449	
Compound	C	H_2O	H_2	
Total energy (hartree)	-38.084	-76.379	-1.164	

1 hartree = 2626.66 kJ·mol^{-1}

We estimated the $\Delta_f H$ for **BPP** from ΔH_{det} based on the above assumed detonation reactions and Hess law [1]. The enthalpies of detonation reaction ($\Delta_c H$) were calculated according to the formula:

$$\Delta_c H = \Delta H_{det} + \Delta nRT,\ (\Delta n = n\ (\text{gaseous products}) - n\ (\text{gaseous reactants})) \quad (5)$$

where, R = 8.314 J·mol^{-1}·K^{-1} and T = 298.15 K. Based on the calculated $\Delta_c H$ and the known $\Delta_f H$ of the products, the $\Delta_f H$ can be calculated from the relevant detonation reactions for molecular perovskite compounds, and the results are listed in Table S7.

Table S7 The enthalpies of formation of compounds, well-known explosives, and the relevant combustion products.

Compound	ΔH_{det} (kJ·mol^{-1})	$\Delta_c H$ (kJ·mol^{-1})	$\Delta_f H$ (kJ·mol^{-1})

RDX	-1241.63	-1223.04	-92.70
HMX	-1652.55	-1627.76	-126.57
BPP	-2609.33	-2572.15	-155.98
CO_2 (g)	—	—	-393.51[a]
H_2O (g)	—	—	-241.826 [a]
N_2 (g)	—	—	0 [a]
HCl (g)	—	—	-92.31 [a]
O_2 (g)	—	—	0[a]
H_2 (g)	—	—	-285.831[a]

[a] The $\Delta_f H$ of the products were derived from National Institute of Standards and Technology (NIST).

After that, the following extended K–J equations were used to calculated the D (km·s^{-1}) and P (GPa) [2]:

$$D = 1.01\Phi^{1/2}(1 + 1.30\rho) \quad (2)$$

$$P = 1.558\Phi\rho^2 \quad (3)$$

$$\Phi = 31.68N(M\Delta H_{det})^{1/2} \quad (4)$$

where, ρ represents the density of explosive (g·cm^{-3}), N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases, and Φ is intermediate parameters.

4. References

[1] Wang, Y.; Zhang, J.; Su, H.; Li, S.; Zhang, S.; Pang, S. A simple method for the prediction of the detonation performances of metal-containing explosives. *J. Phys. Chem. A* **2014**, 118, 4575-4581.

[2] Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys*. **1990**, 92, 508-517.

[3] Monkhorst, H. J.; Pack, J. D. Special points for brillouin-zone integrations. *Phys. Rev. B* **1976**, 13, 5188-5192.

[4] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett*. **1996**, 77, 3865-3868.

5. ^{1}H NMR and ^{13}C NMR Spectra of BPP

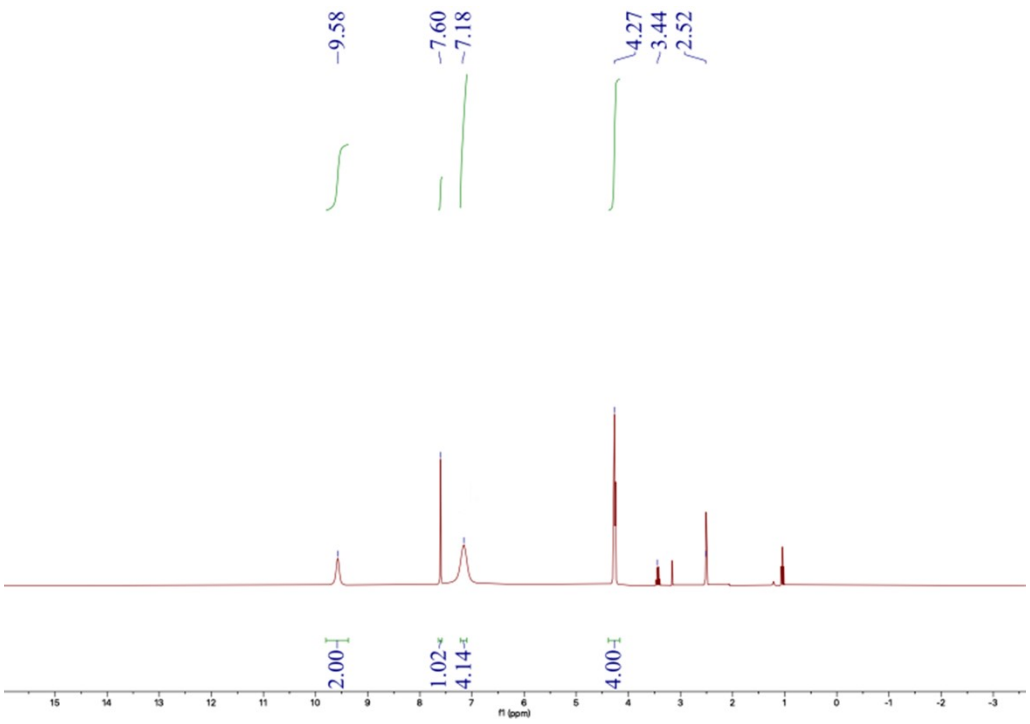

Figure S1 [1]H NMR spectra (300 MHz) of **BPP** in [D6] DMSO at 25 ℃

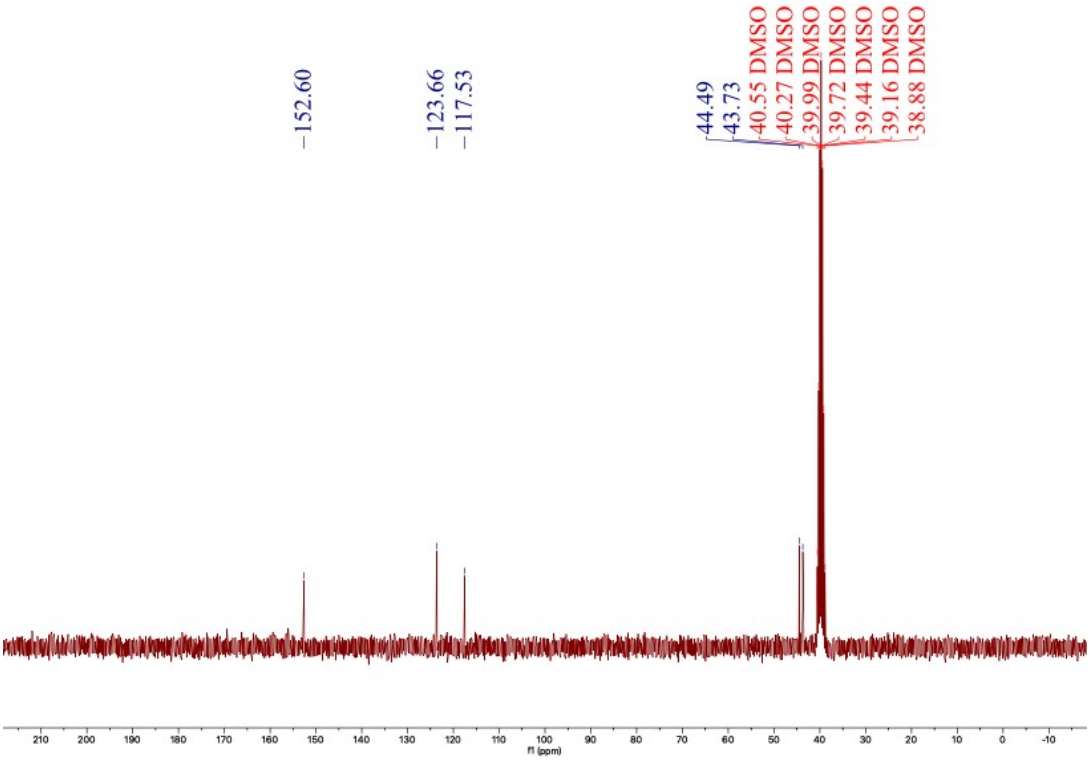

Figure S2 [13]C NMR spectra (75 MHz) of **BPP** in [D6] DMSO at 25 ℃

6. The IR Spectras of BPP

Figure S3 The IR spectra of BPP.

7. The DSC of BPP

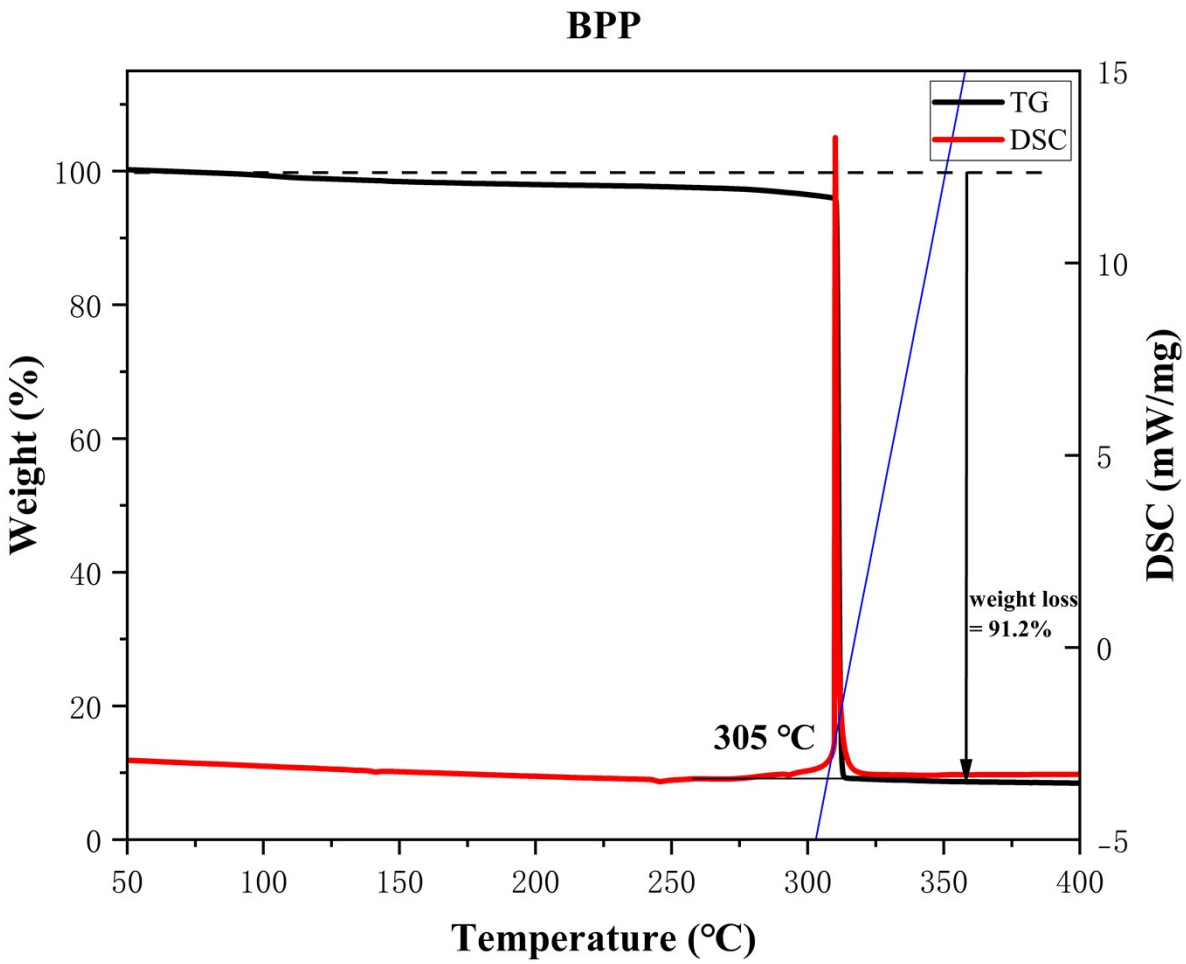

Figure S4 The DSC of **BPP**.