Supporting information

Crystalline modification of energetic salts through polymorphic transition: Enhanced crystal density and energy performance

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Table of contents

1 Experiment section

General methods

All reagents and solvents were purchased from Aladdin and Energy Chemical as analytical grade and were used as received. 1H and 13C NMR spectra were recorded on a Bruker 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for 1H and 13C NMR are reported relative to Me4Si as external standards. The melting and decomposition (onset) points were obtained at a heating rate of 10 ℃ min-1 on a differential scanning calorimeter (Mettler Toledo DSC823e) in closed Al containers with a nitrogen flow of 50ml min-1. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a vario EL Ⅲ CHNOS elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM fallhammer and a BAM friction tester.

Synthesis

Caution: These compounds are dangerous materials, explosions of which may occur in certain conditions. Although we had no difficulties on synthesizing and handing the compounds, proper safety precautions such as safety glasses, plastic spatulas and face shields must be used, especially when the experiments on a large scale.

3-Amino-4-(4,5-diamino-1,2,4-triazole-3-yl)-furazan (**1**): Phosphorus pentoxide (10 g, 70.4 mmol) was slowly added into phosphoric acid (85 wt%,30 g, 260 mmol), and then it was heated to 50°C with stirring. A mixture of 3-amino-4-carboxy furazan (3.87 g, 30mmol) and diaminoguanidine monohydrochloride (6.15 g, 49 mmol) was added to the preheated solution. After addition, the mixture was heated to 120 °C and the evolution of gaseous HCl was observed. The mixture was kept at 120 °C for 5 h and then cooled to room temperature. The ice water (150 ml) was added to the cooled reaction mixture and a white precipitate was formed. The mixture was basified until pH became 8 using conc. NaOH solutions. Then the precipitate was filtered, washed repeatedly with water and air-dried to obtain the crude **1**. Yield: 3.4 g, 62.4 %. ^{1}H NMR (500 MHz, DMSO-d6): δ = 5.91(s), 6.26(s), 6.58(s) ppm. ^{13}C NMR (125.72 MHz, DMSO-d6): δ = 157.18, 154.98, 140.27, 136.58 ppm. IR (KBr): 3435.58, 3351.45, 1690.31, 1608.19, 1403.57, 1379.53, 1340.18, 1183.26, 1045.25, 990.03, 906.71, 769.26, 687.52, 581.31. Elemental analysis of $C_4H_6N_8O$ (182.15): C 26.38, H 3.33, N 61.52 %, found: C 26.46, H 3.28, N 61.31 %.

3-nitramino-4-(4,5-diamino-1,2,4-triazole-3-yl)-furazan (**2**): Nitric acid (68%, 13ml) was cooled to -5°C, then **1** (0.546g, 3mmol) was added in portions keeping the temperature below 0 °C. The mixture was stirred at 0 °C for 15 minutes and then warmed to room temperature. After 24h, the mixture was poured into ice water (20ml). The compound **2** was obtained as a white solid after 1h. Yield: 0.44 g, 65.2 %. ^{1}H

NMR (500 MHz, DMSO-d6): δ= 6.23(br), 8.56(s) ppm. ^{13}C NMR (125.72 MHz, DMSO-d6): δ= 158.25, 151.93, 141.03, 139.59 ppm. IR (KBr): 3662.76, 3476.90, 3367.64, 3336.62, 3112.49, 1704.73, 1642.47, 1582.95, 1506.41, 1468.09, 1419.04, 1371.39, 1273.97, 1187.66, 1101.64, 1046.80, 985.07, 928.23, 872.02, 818.29, 791.64, 777.72, 751.04, 680.92, 656.75, 564.66. Elemental analysis of $C_4H_5N_9O_3$ (227.14): C 21.15, H 2.22, N 55.50 %, found: C 21.22, H 2.19, N 55.61%.

Ammonium 3-nitramino-4-(4,5-diamino-1,2,4-triazole-3-yl)-furazan (**3**): 1.93g of **3** was obtained as a white solid in a yield of 79%. ^{1}H NMR (500 MHz, DMSO-d6): δ = 5.45(s), 6.93(s), 7.36(s) ppm. ^{13}C NMR (125.72MHz, DMSO-d6): δ = 157.64, 156.75, 141.83, 139.66 ppm. IR (KBr): 3574.21, 3358.45, 3193.89, 1655.53, 1619.89, 1589.49, 1556.31, 1518.91, 1442.18, 1389.71, 1271.73, 1092.23, 977.86, 919.97, 880.83, 833.11, 774.70, 748.83, 726.84, 696.40, 591.37. Elemental analysis of $C_4H_8N_{10}O_3$ (244.18): C 19.68, H 3.30, N 57.36 %, found: C 19.73, H 3.26, N 57.43 %.

Polymorphic transition from α-**3** to β-**3**: Kept α-**3** crystals (0.05g, 0.2mmol) in its mother solution and put it in a closed container. Then heated to 80°C within 100 mins and kept it at the same temperature for 3 days. Cooled to the room temperature, colorless needle-shaped crystals (0.038 g, 0.155 mmol) were obtained (yield: 76%, based on α-**3**).

2 X-ray crystallography detail

A colorless cube-shaped crystal (α-**3**) of dimensions 0.35×0.28×0.26 mm^3, a colorless needle-shaped crystal (β-**3**) of dimensions 0.15×0.01×0.01 mm^3 were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-Ka radiation (λ=0.071073 nm). 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). Empirical absorption corrections were applied by using the SADABS (v2008/1) program. The structures were solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands were generated geometrically and refined using a riding model.

Table S1. Crystallographic data.

Compound	α-**3**	β-**3**
CCDC number	1915061	1956858
formula	C4H8N10O3	C4H8N10O3
Mw	244.20	244.20
crystal system	monoclinic	monoclinic
space group	C2/c	$P2_1/c$
a [Å]	18.7451(9)	13.391(2)
b [Å]	7.3716(4)	21.236(3)
c [Å]	14.7077(6)	6.7511(12)
α [°]	90	90
β [°]	110.5010(10)	102.440(6)°
γ [°]	90	90
V [Å^3]	1903.61(16)	1874.7(5)
Z	8	8
T [K]	296	296
λ [Å]	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.704	1.730
μ [mm^{-1}]	0.145	0.147
F [000]	1008	1008
θ range [°]	2.320-27.498	1.829-27.726
GOF on F	1.038	1.082
R_1[I>2σ(I)]	0.0479	0.0854
wR_2[I>2σ(I)]	0.1314	0.2190
R_1[all data]	0.0597	0.1390
wR_2[all data]	0.1393	0.2420

Table S2 Bond lengths [Å] and angles [°] for compound α-**3**

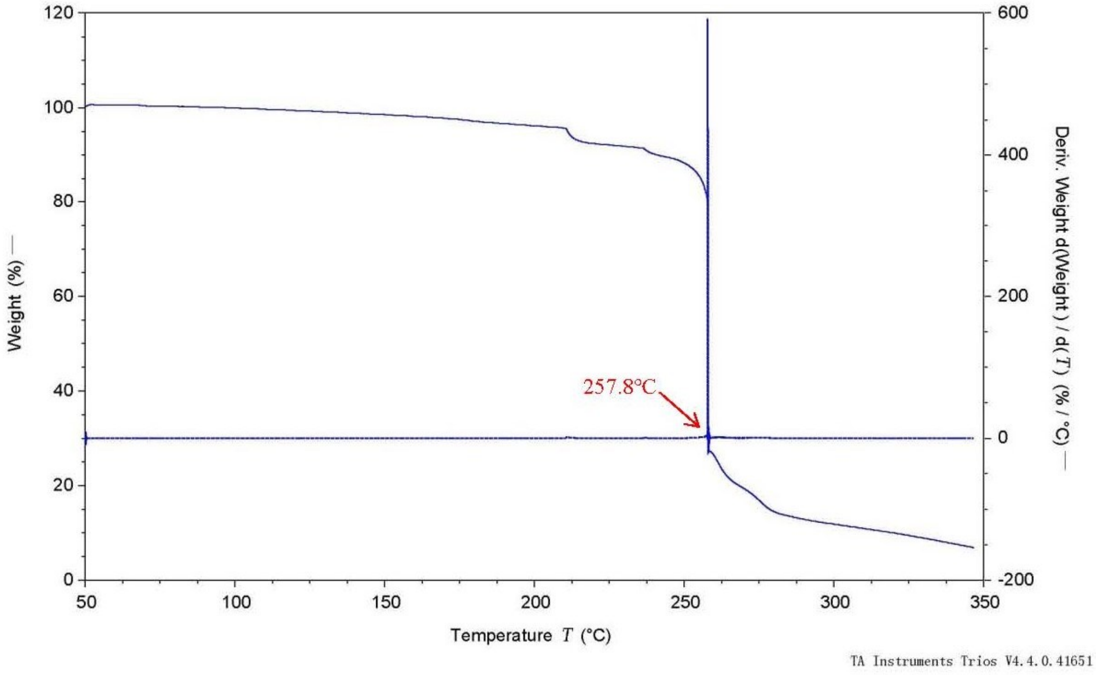
C(1)-N(1)	1.324(2)	N(1)-C(1)-N(8)	128.48(16)
C(1)-N(8)	1.337(2)	N(1)-C(1)-N(3)	109.89(15)
C(1)-N(3)	1.361(2)	N(8)-C(1)-N(3)	121.63(15)
C(2)-N(2)	1.307(2)	N(2)-C(2)-N(3)	109.71(15)
C(2)-N(3)	1.372(2)	N(2)-C(2)-C(3)	126.56(16)
C(2)-C(3)	1.453(2)	N(3)-C(2)-C(3)	123.63(15)
C(3)-N(4)	1.296(2)	N(4)-C(3)-C(4)	109.39(15)
C(3)-C(4)	1.444(2)	N(4)-C(3)-C(2)	121.32(16)
C(4)-N(5)	1.312(2)	C(4)-C(3)-C(2)	129.26(16)
C(4)-N(6)	1.370(2)	N(5)-C(4)-N(6)	131.06(16)
N(1)-N(2)	1.391(2)	N(5)-C(4)-C(3)	108.26(15)
N(3)-N(9)	1.4014(19)	N(6)-C(4)-C(3)	120.62(15)
N(4)-O(1)	1.375(2)	C(1)-N(1)-N(2)	106.86(13)
N(5)-O(1)	1.397(2)	C(2)-N(2)-N(1)	107.92(14)
N(6)-N(7)	1.312(2)	C(1)-N(3)-C(2)	105.61(14)
N(7)-O(3)	1.238(2)	C(1)-N(3)-N(9)	122.38(14)
N(7)-O(2)	1.270(2)	C(2)-N(3)-N(9)	131.91(14)
N(8)-H(8A)	0.8600	C(3)-N(4)-O(1)	105.96(14)
N(8)-H(8B)	0.8600	C(4)-N(5)-O(1)	105.28(14)
N(9)-H(9A)	0.8600	N(7)-N(6)-C(4)	116.53(15)
N(9)-H(9B)	0.8600	O(3)-N(7)-O(2)	119.96(15)
N(10)-H(10A)	0.9212	O(3)-N(7)-N(6)	124.49(16)
N(10)-H(10B)	1.0182	O(2)-N(7)-N(6)	115.56(15)
N(10)-H(10C)	0.9582	C(1)-N(8)-H(8A)	120.0
N(10)-H(10D)	0.9990	C(1)-N(8)-H(8B)	120.0
		H(8A)-N(8)-H(8B)	120.0
		N(3)-N(9)-H(9A)	120.0
		N(3)-N(9)-H(9B)	120.0
		H(9A)-N(9)-H(9B)	120.0
		H(10A)-N(10)-H(10B)	108.8
		H(10A)-N(10)-H(10C)	112.4
		H(10B)-N(10)-H(10C)	110.4
		H(10A)-N(10)-H(10D)	109.1
		H(10B)-N(10)-H(10D)	104.9
		H(10C)-N(10)-H(10D)	110.9
		N(4)-O(1)-N(5)	111.10(12)

Table S3 Bond lengths [Å] and angles [°] for compound β-**3**

C(1)-N(1)	1.309(6)	N(1)-C(1)-N(8)	127.2(4)
C(1)-N(8)	1.339(6)	N(1)-C(1)-N(3)	110.0(4)
C(1)-N(3)	1.365(6)	N(8)-C(1)-N(3)	122.8(4)
C(2)-N(2)	1.311(5)	N(2)-C(2)-N(3)	109.4(4)
C(2)-N(3)	1.361(5)	N(2)-C(2)-C(3)	126.6(4)
C(2)-C(3)	1.455(6)	N(3)-C(2)-C(3)	124.0(4)
C(3)-N(4)	1.290(6)	N(4)-C(3)-C(4)	110.0(4)
C(3)-C(4)	1.447(6)	N(4)-C(3)-C(2)	121.2(4)
C(4)-N(5)	1.302(5)	C(4)-C(3)-C(2)	128.7(4)
C(4)-N(6)	1.370(5)	N(5)-C(4)-N(6)	131.3(4)
C(5)-N(10)	1.325(5)	N(5)-C(4)-C(3)	107.9(4)
C(5)-N(17)	1.339(5)	N(6)-C(4)-C(3)	120.8(4)
C(5)-N(12)	1.347(5)	N(10)-C(5)-N(17)	126.3(4)
C(6)-N(11)	1.302(5)	N(10)-C(5)-N(12)	110.2(3)
C(6)-N(12)	1.384(5)	N(17)-C(5)-N(12)	123.4(4)
C(6)-C(7)	1.458(6)	N(11)-C(6)-N(12)	109.1(3)
C(7)-N(13)	1.296(5)	N(11)-C(6)-C(7)	126.2(4)
C(7)-C(8)	1.436(6)	N(12)-C(6)-C(7)	124.7(3)
C(8)-N(14)	1.312(5)	N(13)-C(7)-C(8)	109.4(4)
C(8)-N(15)	1.373(5)	N(13)-C(7)-C(6)	122.0(4)
N(1)-N(2)	1.392(5)	C(8)-C(7)-C(6)	128.6(4)
N(3)-N(9)	1.397(5)	N(14)-C(8)-N(15)	130.9(4)
N(4)-O(1)	1.379(5)	N(14)-C(8)-C(7)	108.2(4)
N(5)-O(1)	1.397(5)	N(15)-C(8)-C(7)	120.9(3)
N(6)-N(7)	1.333(5)	C(1)-N(1)-N(2)	106.9(3)
N(7)-O(2)	1.237(5)	C(2)-N(2)-N(1)	107.9(3)
N(7)-O(3)	1.249(5)	C(2)-N(3)-C(1)	105.8(3)
N(8)-H(8A)	0.8600	C(2)-N(3)-N(9)	131.8(4)
N(8)-H(8B)	0.8600	C(1)-N(3)-N(9)	122.3(3)
N(9)-H(9A)	0.8600	C(3)-N(4)-O(1)	105.3(3)
N(9)-H(9B)	0.8600	C(4)-N(5)-O(1)	105.6(3)
N(10)-N(11)	1.386(5)	N(7)-N(6)-C(4)	116.7(3)
N(12)-N(18)	1.407(5)	O(2)-N(7)-O(3)	120.9(4)
N(13)-O(4)	1.371(5)	O(2)-N(7)-N(6)	123.6(4)
N(14)-O(4)	1.396(5)	O(3)-N(7)-N(6)	115.5(4)
N(15)-N(16)	1.309(5)	C(1)-N(8)-H(8A)	120.0
N(16)-O(6)	1.246(4)	C(1)-N(8)-H(8B)	120.0
N(16)-O(5)	1.271(4)	H(8A)-N(8)-H(8B)	120.0
N(17)-H(17A)	0.8600	N(3)-N(9)-H(9A)	120.0
N(17)-H(17B)	0.8600	N(3)-N(9)-H(9B)	120.0
N(18)-H(18A)	0.8600	H(9A)-N(9)-H(9B)	120.0
N(18)-H(18B)	0.8600	C(5)-N(10)-N(11)	106.6(3)

N(19)-H(19A)	0.8745	C(6)-N(11)-N(10)	108.4(3)
N(19)-H(19B)	0.8197	C(5)-N(12)-C(6)	105.6(3)
N(19)-H(19C)	0.7856	C(5)-N(12)-N(18)	124.2(3)
N(19)-H(19D)	0.8986	C(6)-N(12)-N(18)	130.1(3)
N(20)-H(20D)	0.8999	C(7)-N(13)-O(4)	106.1(3)
N(20)-H(20A)	0.9000	C(8)-N(14)-O(4)	105.4(3)
N(20)-H(20B)	0.9000	N(16)-N(15)-C(8)	116.7(3)
N(20)-H(20C)	0.9000	O(6)-N(16)-O(5)	119.7(3)
		O(6)-N(16)-N(15)	125.1(3)
		O(5)-N(16)-N(15)	115.2(3)
		C(5)-N(17)-H(17A)	120.0
		C(5)-N(17)-H(17B)	120.0
		H(17A)-N(17)-H(17B)	120.0
		N(12)-N(18)-H(18A)	120.0
		N(12)-N(18)-H(18B)	120.0
		H(18A)-N(18)-H(18B)	120.0
		H(19A)-N(19)-H(19B)	87.4
		H(19A)-N(19)-H(19C)	104.8
		H(19B)-N(19)-H(19C)	112.2
		H(19A)-N(19)-H(19D)	126.1
		H(19B)-N(19)-H(19D)	125.1
		H(19C)-N(19)-H(19D)	100.3
		H(20D)-N(20)-H(20A)	109.5
		H(20D)-N(20)-H(20B)	109.5
		H(20A)-N(20)-H(20B)	109.5
		H(20D)-N(20)-H(20C)	109.5
		H(20A)-N(20)-H(20C)	109.5
		H(20B)-N(20)-H(20C)	109.5
		N(4)-O(1)-N(5)	111.1(3)
		N(13)-O(4)-N(14)	110.8(3)

3 TGA-DTA curves



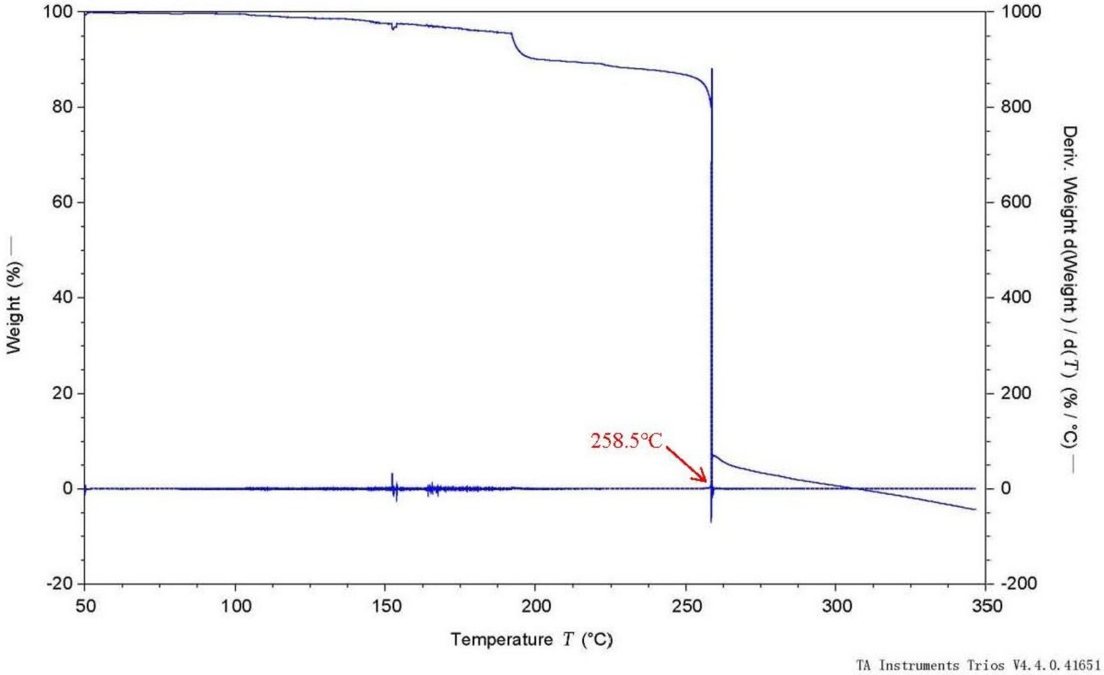
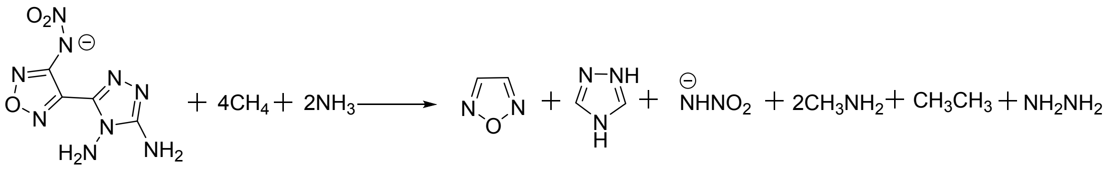


Figure S1 The TGA-DTA curves of α-**3** (top) and β-**3** (bottom)**.**

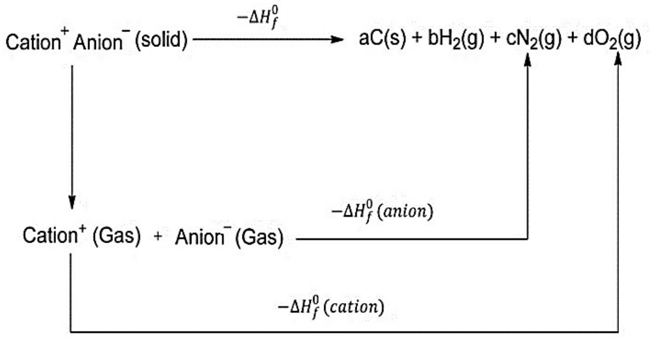
4 Theoretical study

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs.[1] The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method.



Scheme S1. Isodesmic reactions

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Scheme S2) [2]. The number is simplified by equation 1:



Scheme S2. Born-Haber Cycle for the formation of energetic salts.

$$\mathbf{\Delta Hf^{o}\ (salt,\ 298\ K) = \Delta Hf^{o}\ (cation,\ 298K) + \Delta Hf^{o}\ (anion,\ 298K) - \Delta H_L} \qquad \mathbf{(1)}$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.[2] [Eq. (2)]

$$\mathbf{\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT} \qquad \mathbf{(2)}$$

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-}, respectively. The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

$$\mathbf{U_{POT}\ [kJ\ mol^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta} \qquad \mathbf{(3)}$$

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for (g) and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature[3, 4], the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\mathbf{\Delta H_{sub} = 188/J\ mol^{-1}K^{-1} \times T}$$

The binding energy is the difference between the total energy of the system and individual monomers, which can reflect the component compatibility in the system. Gaussian 09 package was used to perform molecular orbital calculations under DFT-

B3LYP method with 6-31++ G (d,p) basis set.The binding energy was calculated using the following equation.[5]

$$\mathbf{E_{int} = E_{tot} - E_A - E_B + E_{BSSE}}$$

5 References

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