

Supporting Information

**Achieving Ultra-High Heat Resistance of Novel Energetic Materials through  
Hydrogen Bonding and Extended  $\pi$ -Conjugation Strategy**

<sup>‡</sup>Xiue Jiang, <sup>‡</sup>Dangyue Yin, Siwei Song, Yi Wang\*, Mingren Fan, Ruihui Wang, Qinghua Zhang\*

School of Astronautics, Northwestern Polytechnical University, Shanxi Xi'an, 710065, China

<sup>‡</sup>These authors contributed equally to this work.

\* E-mail address: [ywang0521@nwpu.edu.cn](mailto:ywang0521@nwpu.edu.cn) (Yi Wang); [qinghuazhang@nwpu.edu.cn](mailto:qinghuazhang@nwpu.edu.cn)

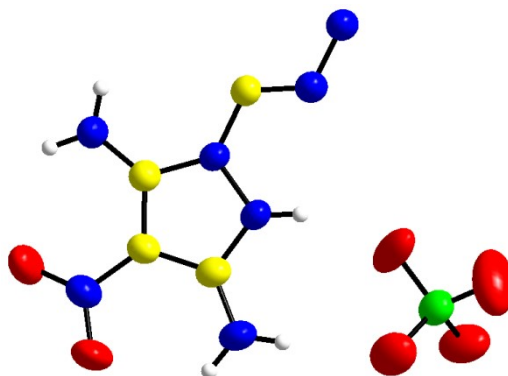
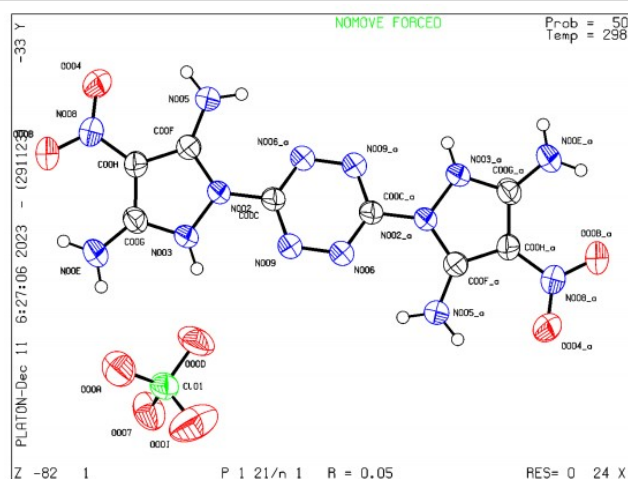
(Qinghua Zhang)

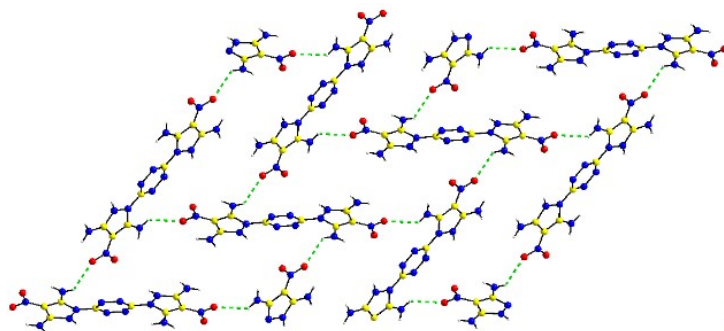
Table of content

Crystallographic data and ellipsoid plot for <b>NPX-01</b> ·2HClO <sub>4</sub> .....	S1-S2
Crystallographic data and ellipsoid plot for <b>NPX-02</b> ·2HClO <sub>4</sub> .....	S3-S4
Ozawa curves of <b>NPX-01</b> and <b>NPX-02</b> .....	S5
<sup>13</sup> C NMR spectra of <b>NPX-01</b> .....	S5
<sup>13</sup> C NMR spectra of <b>NPX-02</b> .....	S5
DSC curves of <b>NPX-01</b> ·2HClO <sub>4</sub> and <b>NPX-02</b> ·2HClO <sub>4</sub> .....	S6
Calculation procedures for heat of formation.....	S6-7
Reference.....	S7

**Table S1.** Crystallographic data and ellipsoid plot for **NPX-01**·2HClO<sub>4</sub>

Crystals	NPX-01·2HClO <sub>4</sub>
CCDC	2338599
Formula	C <sub>8</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>14</sub> O <sub>12</sub>
Formula weight	565.20
Temperature	298.15 K
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
$\rho/g \cdot \text{cm}^{-3}$	1.802
<i>a</i> /Å	6.1365(2)
<i>b</i> /Å	13.3475(4)
<i>c</i> /Å	12.6025(4)
$\alpha$ (°)	90
$\beta$ (°)	92.164(3)
$\gamma$ (°)	90
Goodness-of-fit on F <sup>2</sup>	1.084
R	0.0497
wR	0.1455

**Figure S1.** The asymmetric unit of **NPX-01**·2HClO<sub>4</sub>.



**Figure S2.** The layer structure contained in **NPX-01** cations.

**Table S2** The torsion angles of compound **NPX-01**·2HClO<sub>4</sub>

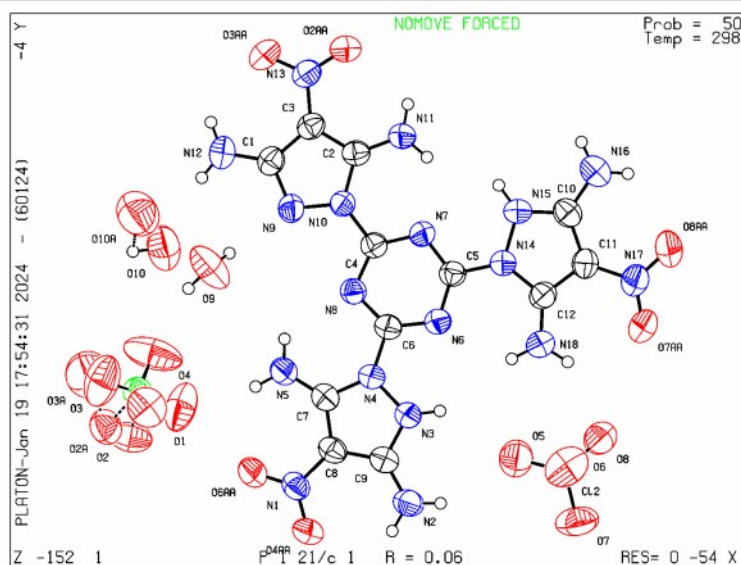
Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
C00C-N002-N003-C00G	176.2(2)	C00F-N002-N003-C00G	5.7(3)
N003-N002-C00C-N006_a	170.1(2)	C00F-N002-C00C-N009	159.2(3)
N003-N002-C00F-N005	176.0(2)	N003-N002-C00F-C00H	-3.8(3)
C00C-N002-C00F-C00H	-172.7(2)	N002-N003-C00G-N00E	174.2(2)
C00C_a-N006-N009-C00C	0.2(4)	N002-N003-C00G-C00H	-5.1(3)
O004-N008-C00H-C00F	0.6(4)	O004-N008-C00H-C00G	-177.5(3)
O00B-N008-C00H-C00G	2.8(4)	N006-N009-C00C-N002	178.6(2)
N002-C00F-C00H-N008	-177.8(2)	N002-C00F-C00H-C00G	0.6(3)
N005-C00F-C00H-C00G	-179.1(3)	N003-C00G-C00H-N008	-178.8(2)
N00E-C00G-C00H-N008	2.0(5)	N00E-C00G-C00H-C00F	-176.4(3)
N003-N002-C00C-N009	-8.9(3)	O00B-N008-C00H-C00F	-179.1(3)
C00F-N002-C00C-N006_a	-21.8(4)	N006-N009-C00C-N006_a	-0.3(4)
C00C-N002-C00F-N005	7.0(4)	N005-C00F-C00H-N008	2.5(5)
N009-N006-C00C_a-N009_a	-0.3(4)	N003-C00G-C00H-C00F	2.9(3)

**Table S3** Hydrogen bonds of compound **NPX-01**·2HClO<sub>4</sub>

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/ °
N003-H003···O00D	0.86	2.08	2.784(3)	139
N005-H00A···O00B	0.86	2.4	3.056(3)	133
N005-H00A···N006	0.86	2.24	2.827(3)	126
N005-H00B···O004	0.86	2.28	2.816(3)	121
N005-H00B···O00I	0.86	2.3	3.102(5)	156
N00E-H00C···O00A	0.86	2.11	2.968(4)	176
N00E-H00D···O00B	0.86	2.24	2.781(4)	121
N00E-H00D···O007	0.86	2.31	3.087(4)	150

**Table S4.** Crystallographic data and ellipsoid plot for **NPX-02·2HClO<sub>4</sub>**

Crystals	NPX-02·2HClO <sub>4</sub>
CCDC	2338600
Formula	C <sub>12</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>18</sub> O <sub>16</sub>
Formula weight	741.34
Temperature	298.15 K
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
$\rho/g \cdot cm^{-1}$	1.856
<i>a</i> /Å	14.8517(3)
<i>b</i> /Å	15.5923(3)
<i>c</i> /Å	12.3844(2)
$\alpha/^\circ$	90
$\beta/^\circ$	112.337(2)
$\gamma/^\circ$	90
Goodness-of-fit on F <sup>2</sup>	1.043
R	0.0645
wR	0.2095



**Table S5** The torsion angles of compound **NPX-02**·2HClO<sub>4</sub>

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
O4AA-N1-C8-C7	-176.3(3)	N9-C1-C3-N13	-179.9(3)
O6AA-N1-C8-C9	-177.1(3)	N12-C1-C3-C2	179.2(3)
N4-N3-C9-N2	-176.9(3)	N11-C2-C3-N13	-3.6(6)
N3-N4-C6-N8	174.2(2)	N4-C7-C8-C9	0.8(3)
N3-N4-C7-N5	-178.7(3)	N1-C8-C9-N2	-1.5(6)
O3AA-N13-C3-C2	179.9(3)	C7-C8-C9-N3	-3.0(4)
C5-N6-C6-N4	-178.0(3)	N16-C10-C11-N17	-2.6(6)
C5-N7-C4-N10	178.2(3)	N17-C11-C12-N18	0.2(6)
C6-N8-C4-N7	2.6(4)	O4AA-N1-C8-C9	3.1(5)
C4-N8-C6-N6	-3.0(4)	C9-N3-N4-C6	-170.4(3)
N10-N9-C1-N12	-176.7(3)	N4-N3-C9-C8	4.0(3)
N9-N10-C2-C3	4.1(3)	C7-N4-C6-N6	-170.5(3)
N9-N10-C4-N7	174.1(3)	N3-N4-C7-C8	1.7(3)
C2-N10-C4-N8	178.6(3)	C6-N6-C5-N7	2.4(4)
O3AA-N13-C3-C1	-2.3(5)	C5-N6-C6-N8	0.8(4)
C12-N14-N15-C10	-1.3(4)	C4-N7-C5-N6	-2.7(5)
C12-N14-C5-N6	3.7(5)	C6-N8-C4-N10	-175.6(3)
N15-N14-C12-C11	0.9(4)	C1-N9-N10-C2	-5.4(3)
N14-N15-C10-N16	-178.3(3)	N10-N9-C1-C3	4.3(4)
O7AA-N17-C11-C12	4.0(5)	C4-N10-C2-N11	-1.0(5)

**Table S6** Hydrogen bonds of compound **NPX-02**·2HClO<sub>4</sub>

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/ °
N2-H2A···O5	0.86	2.33	3.086(5)	146
N2-H2B···O4AA	0.86	2.26	2.804(4)	121
N2-H2B···O6	0.86	2.28	3.052(6)	150
N3-H3···O5	0.86	2.38	3.085(6)	139
N3-H3···O4AA	0.86	2.46	2.935(4)	116
N5-H5A···N8	0.86	2.22	2.808(4)	126
N5-H5A···O2	0.86	2.56	2.946(6)	108
N5-H5B···O1	0.86	2.28	3.011(7)	142
N5-H5B···O6AA	0.86	2.29	2.825(4)	121
O9-H9A···N9	0.89	2.03	2.696(6)	131
O9-H9B···O4	0.85	2.07	2.891(6)	164
O10-H10A···N15	0.85	2.41	3.150(8)	145
O10-H10B···O9	0.85	2.04	2.786(9)	145
N11-H11A···N7	0.86	2.04	2.642(4)	126
N11-H11B···O2AA	0.86	2.21	2.758(4)	122
N11-H11B···O1	0.86	2.13	2.928(6)	154
N12-H12A···O8	0.86	2.58	3.188(5)	129

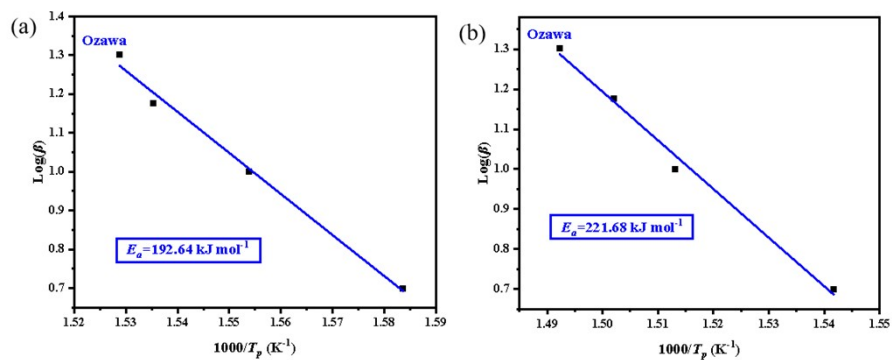


Figure S3. Ozawa curves of NPX-01 (a) and NPX-02 (b).

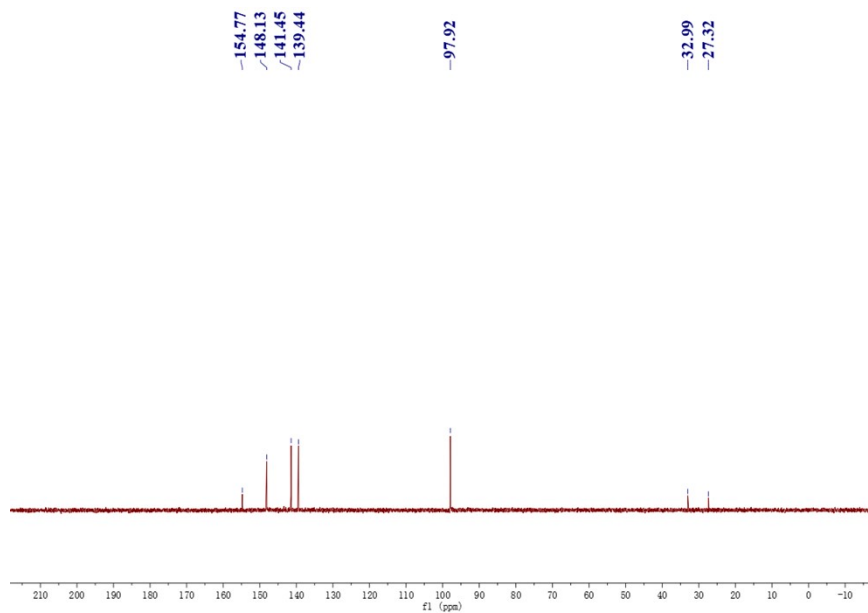


Figure S4.  $^{13}\text{C}$  NMR of NPX-01 ( $\text{D}_2\text{SO}_4-d_2$ )

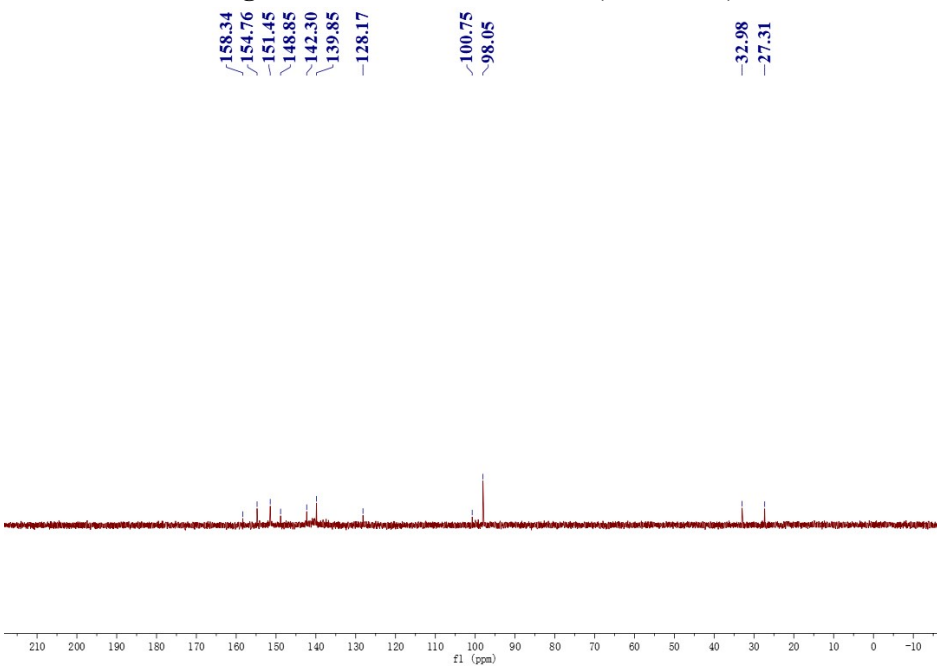
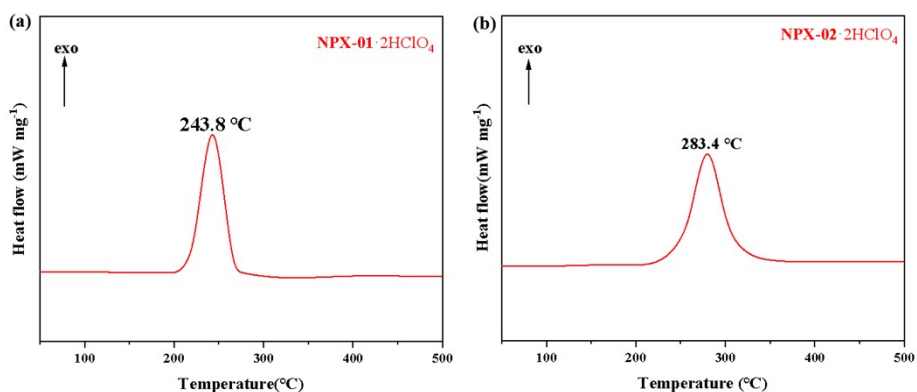


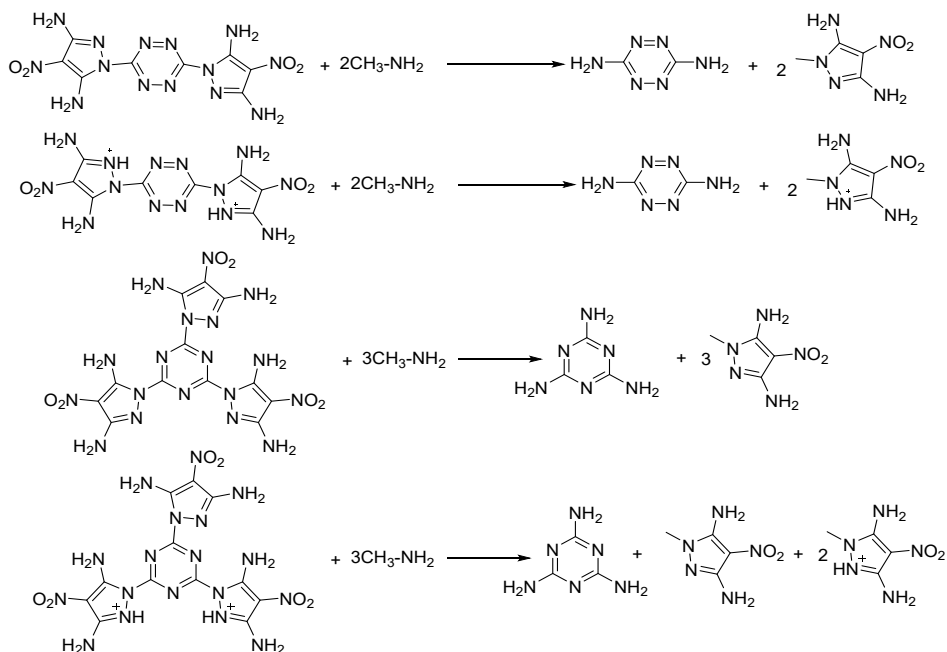
Figure S5.  $^{13}\text{C}$  NMR of NPX-02 ( $\text{D}_2\text{SO}_4-d_2$ )



**Figure S6.** DSC curves of (a) NPX-01·2HClO<sub>4</sub> (b) NPX-02·2HClO<sub>4</sub>

### Calculation procedures for heat of formation

Computations were carried out by using the Gaussian09 suite of programs.<sup>[1]</sup> The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals<sup>[2]</sup> with 6-31+G\*\* basis set.<sup>[3]</sup> All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Then, the single-point energies of optimized structures were accessed under the level of MP2/6-311++G\*\*. The predictions of heats of formation (HOF) were implemented via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of these compounds are in Scheme S1.



**Scheme S1.** Isodesmic reaction for computing the HOF

The change of enthalpy for the reactions at 298 K can be expressed as:

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \quad (1)$$

Where  $\Delta_f H_R$  and  $\Delta_f H_P$  are the HOF of reactants and products at 298 K, respectively, and

$\Delta H_{298}$  can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

Where  $E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies ( $ZPE$ ) of the products and the reactants at 0 K;  $\Delta H_T$  is thermal correction from 0 to 298 K. The  $\Delta(PV)$  value in eq (2) is the  $PV$  work term. It equals  $\Delta nRT$  for the reactions of ideal gas. For the isodesmic reactions,  $\Delta n = 0$ , so  $\Delta(PV) = 0$ . On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from the experiments<sup>[4-6]</sup> or from the high level computing like G4(MP2)-6x<sup>[7]</sup>.

For ionic energetic compounds, the HOF can be simplified by eq 3:

$$\Delta H_f^\theta(\text{salt}, 298 \text{ K}) = \Delta H_f^\theta(\text{cation}, 298 \text{ K}) + \Delta H_f^\theta(\text{anion}, 298 \text{ K}) - \Delta H_L \quad (3)$$

where  $\Delta H_L$  is the lattice energy of the salts that can be predicted by the formula suggested by Jenkins et al. as:

$$\Delta H_L = U_{\text{POT}} + [p(nM/2 - 2) + q(nX/2 - 2)]RT \quad (4)$$

where  $nM$  and  $nX$  depend on the nature of the ions  $M^{p+}$  and  $X^{q-}$ , respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy  $U_{\text{POT}}$  ( $\text{kJ mol}^{-1}$ ) is as follows:

$$U_{\text{POT}} (\text{kJ mol}^{-1}) = \gamma (\rho_m/M_m)^{1/3} + \delta \quad (5)$$

where  $\rho$  ( $\text{g cm}^{-3}$ ) is the density and  $M$  ( $\text{g mol}^{-1}$ ) is the chemical formula mass of the ionic material. For 1:1 (charge ratio) salts, the coefficients  $\gamma$  and  $\delta$  are  $1981.2 \text{ kJ mol}^{-1} \cdot \text{cm}$  and  $103.8 \text{ kJ mol}^{-1}$ , respectively.<sup>[8]</sup>

## Reference

- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09, Gaussian, Inc. Wallingford, CT: 2009.
- [2] A. D. Becke. Density-functional thermochemistry. III. The role of exact exchange. *J Phys Chem*, 1993, 98, 5648-5652; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J Phys Chem*, 1994, 98, 11623-11627.
- [3] P. C. Hariharan, J. A. Pople. The influence of polarization functions on molecular orbital hydrogenation energies. *Theoretica Chimica Acta*, 1973, 28, 213-222.
- [4] a) M. W. Schmidt, M. S. Gordon, J. A. Boatz. Triazolium-Based Energetic Ionic Liquids. *J Phys Chem A*, 2005, 109, 7285-7295; b) H. Gao, C. Ye, C. M. Piekarski, et al. Computational characterization of energetic salts. *J Phys Chem C*, 2007, 111, 28, 10718-10731.
- [5] M. Jaidann, S. Roy, H. Abou-Rachid, et al. A DFT theoretical study of heats of formation and detonation properties of nitrogen-rich explosives. *J Hazard Mater*, 2010, 176, 165-173.
- [6] J. A. Pople. J. S. Binkley, R. Seeger. Theoretical models incorporating electron correlation. *Int J Quantum Chem*, 1976, 10, 1-19.
- [7] B. Chan, J. Deng, L. Radom. G4 (MP2)-6X: A cost-effective improvement to G4 (MP2). *J Chem Theory Comput*, 2011, 7, 112-120.
- [8] X. Xu, H. Xiao, X. Ju, et al. Computational Studies on Polynitrohexaaz- aadamantanes as Potential High Energy Density Materials. *J Phys Chem A*, 2006, 110, 5929- 5933; b) G. Wang, X. Gong, L. Yiu, et al. A theoretical investigation on the structures, densities, detonation properties and pyrolysis mechanism of the nitro derivatives of toluenes. *J Hazard Mater*, 2010, 177, 703-710.