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Cover Page Footnote

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The Explosive Sensitivity on the Complex Formation of 3-Nitro-1,2,4-Triazol-5-One and Metal Ions Based on Density Functional Study

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Abstract

The explosive sensitivity upon the formation of supramolecular interaction between the nitro group of 3-nitro-1,2,4-triazol-5-one (NTO) and metal ions ($M^{n+} = Li^+, Na^+, Be^{2+}$ and Mg^{2+}) has been investigated using Density Functional Theory at B3LYP/6-311++G** level of theory. The bond dissociation energy (BDE) of the C1–N6 trigger bond has also been discussed for the NTO monomer and the corresponding complexes. The interaction and bond dissociation energy of the C6–N7 trigger bond follow the order of $NTO-Be^{2+} > NTO-Mg^{2+} > NTO-Li^+ > NTO-Na^+ > NTO$ monomer. The enhancement of the trigger bond dissociation energy in comparison with the NTO monomer correlates well with the complex interaction energies, trigger bond length, and charge transfer. The analyses of electron density shifts have shown that the electron density of the nitro group shifts toward the C1–N6 trigger bond upon the formation of the supramolecular interaction. As result, the trigger bond is strengthened and the sensitivity of NTO is reduced. Some of the calculated results agree with the experimental values.

Abstrak

Sensitivitas Peledak Akibat Pembentukan Kompleks 3-Nitro-1,2,4-Triazol-5-One dan Ion Logam berdasarkan Teori Fungsional Kerapatan. Sensitivitas peledak yang terbentuk dari interaksi supramolekuler senyawa 3-nitro-1,2,4-triazol-5-one (NTO) dan ion logam ($M^{n+} = Li^+, Na^+, Be^{2+}$ and Mg^{2+}) telah dipelajari menggunakan Teori Fungsional Kerapatan pada tingkatan teori B3LYP/6-311++G**. Energi pemutusan ikatan pada ikatan pemicu ledakan (C1–C6) juga telah dipelajari untuk monomer NTO dan senyawa kompleksnya. Energi ikat dan energi pemutusan ikatan mengikuti urutan: $NTO-Be^{2+} > NTO-Mg^{2+} > NTO-Li^+ > NTO-Na^+ > monomer NTO$. Peningkatan energi pemutusan ikatan berbanding lurus dengan energi ikat, panjang ikatan pemicu ledakan dan transfer muatan. Analisis perubahan kerapatan elektron menunjukkan bahwa kerapatan elektron gugus nitro berpindah pada ikatan C1–N6 ketika kompleks terbentuk. Hal ini menyebabkan ikatan pemicu ledakan menjadi semakin kuat sehingga sensitivitas NTO menjadi berkurang. Hasil kajian teoritis ini sesuai dengan hasil kajian eksperimen.

Keywords: density functional theory, explosive, sensitivity

Introduction

The effort to reduce hazards caused by munitions has been a major focus for decades, especially when production processes, storage, transportation, and handling during conflict and peacetime are concerned. The importance of increasing the safety during conflict has been displayed by involving munitions, and massive disasters have also involved military storage and ground transportation. As a consequence, in many cases the accidents caused by munitions are often devastating,

causing not only severe damage to the equipment and combat platforms but also loss of human lives. Therefore, it is reasonable to develop technologies that are able to reduce the risk associated with munitions. An example of such technology is a new type of munitions with low vulnerability called Insensitive Munitions (IM). One approach for creating explosive formulation IM requirements is the use of insensitive energetic materials, which for IM can be shown in NTO based formulations, such as metal salts of NTO and its inclusion compounds [1,2].

Interaction of NTO with metal ions has been the subject of many studies, ranging from the preparation process and thermal studies to explosive characteristics. This interaction is shown by the metal salts of NTO, which include transition metals, alkali and alkaline earth metals, rare metals, and metal complexes. A range of alkali and heavy metals was synthesized for evaluating these compounds as potential primary explosives. These salts included the sodium, potassium, silver, lead, mercuric, barium, cadmium, strontium, cupric, nickel, and stannous salts, as well as acid derivatives. The study indicated that these salts exhibited the sensitivity of secondary explosives, as they were difficult to explode, and would not be suitable for primary explosives [1,3].

In the area of explosive characteristics, the sensitivity of explosives indicates the effect of stability to various external stimuli such as heat, impact, shock, and electric spark. Prediction of the sensitivity, which can be approached from molecular structure, is a very important step for developing new energetic materials. Therefore, sensitivity measurements are important. However, the experimental study of such properties is hazardous, time consuming, and expensive. Rapid development in the area of computational chemistry provides a solution for this difficulty.

Many theoretical studies have shown that sensitivity of the explosive compounds has a good linear relationship with the trigger BDE or the charge transfer of the nitro group. In particular, it has been confirmed that the intermolecular interaction can reduce the explosive sensitivity. Many studies of the intermolecular interaction process have proved that molecule-cation interaction is one of the strongest interactions [4–9]. This leads to the conclusion that the molecule-cation interaction may be responsible for reducing explosive sensitivity.

Molecular dynamic simulation of unimolecular decomposition of the NTO molecule indicated that C-NO₂ undergoes the homolysis [10]. Du *et al.* [11] performed the first theoretical calculation in order to study the explosive sensitivity upon the formation of molecule-cation interaction between the nitro group of 3,4-dinitroprazole (DNP) and alkaline and alkaline earth cations. They investigated the explosive sensitivity using the B3LYP and MP2(full) methods with the 6-311++G** and 6-311++G(2df,2p) basis sets. The theoretical investigation of the explosive sensitivity upon the formation of the Na⁺ complexes with nitrotriazole or its methyl derivatives has also been reported [12]. Recently, Li *et al.* [13] investigated the influence of the intermolecular H-bonding interaction on the strength of the C–NO₂ bond in nitrotriazoles in the change of explosive sensitivity. To the authors' knowledge, no investigation into the effect of the molecule-cation interaction on the explosive sensitivity or the BDE of the nitro group of NTO has been presented. This study

also analyzed the changes of the bond length and bond dissociation energy of the trigger bond as well as the nitro group and cation charge upon the formation of the molecule-cation interaction.

Materials and Methods

All density functional theory calculations were performed with NWChem suit of quantum chemistry code [20]. The complex structures were optimized using DFT at B3LYP level of calculation. All calculations used 6-31++G** basis set. The optimized structures in all cases corresponded to the minimum energy point of the PES (potential energy surface) because no imaginary frequencies were found. The BDE of the C–NO₂ bond was calculated and defined as:

$$\text{BDE} = E_{\text{NO}_2\text{-M}^{\text{n+}}} + E_{\text{R}} - E_{\text{RNO}_2\text{-M}^{\text{n+}}} \quad (1)$$

R is 1,2,4-triazol-5-one radical. Mⁿ⁺ is Li⁺, Na⁺, Be²⁺ and Mg²⁺.

Molecule-cation interaction (E_{int}) was investigated with the definition of the energy difference between the complex and isolated monomer.

$$E_{\text{int}} = E_{\text{NTO-M}^{\text{n+}}} - E_{\text{NTO}} - E_{\text{M}} \quad (2)$$

Results and Discussion

Geometries. The quality of the computational level was assessed by optimizing the NTO molecule and comparing the structural parameters with X-ray data. For this purpose, the density functional theory using B3LYP/6-31G++** level of theory was tested for NTO atoms. The comparison between calculated bond length and the experimental X-ray results on the same structure [14] is depicted in Table 1. In Figure 1, the calculated optimized structure of NTO is presented.

The calculated bond length values agree with the experimental values, although B3LYP/6-31++G** predicts the distance between atoms of NTO is 0.01 – 0.04 Å longer than those of the X-ray structure. This data indicates that the B3LYP/6-31++G** provides an

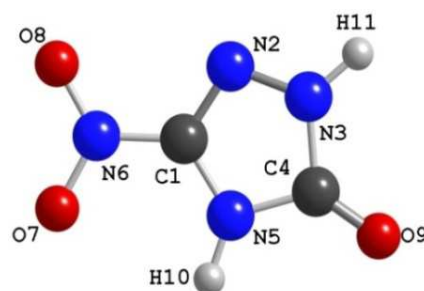


Figure 1. Optimized NTO Structure at B3LYP/6-31++G Level of Theory. Black is Carbon, Blue is Nitrogen, Red is Oxygen, and White is a Hydrogen Atom**

accurate prediction of the structural parameter of the NTO molecule. Based on the bond length data in Table 1, the preliminary calculation of bond length of NTO, the C1-N6 bond is the longest bond in the NTO molecule, indicating that it is the weakest bond in the NTO molecule and is considered the trigger bond. It is also strengthened by the previous report, which indicated that for nitro group explosives, the weakest bonds O-NO₂, N-NO₂ and C-NO₂ are the trigger bonds [15]. Thus, the current work focuses on the C1-N6 trigger bond with its correlation toward sensitivity of NTO explosive and the influence of supramolecular interaction between NTO and metal ions (Li⁺, Na⁺, Be²⁺, Mg²⁺) through the complex sensitivity.

In order to study the effect of metal ions on the sensitivity of NTO molecules, the metal ions (Li⁺, Na⁺, Be²⁺, Mg²⁺) were incorporated into the nitro functional position of NTO. The geometric parameters of these complexes are depicted in Table 2. It was noted that the bond lengths of C1-N6 decrease after interaction with metal ions in comparison with those in the NTO monomer. The calculated bond lengths showed that the bond length reduction is 0.011 Å, 0.004 Å, 0.115 Å, 0.105 Å in NTO-Li⁺, NTO-Na⁺, NTO-Be²⁺, NTO-Mg²⁺ respectively. The decrease of bond length follows the order of NTO-Be²⁺ > NTO-Mg²⁺ > NTO-Li⁺ > NTO-Na⁺. In general, this bond length reduction trend shows that the trigger bond C1-N6 is strengthened in NTO-cation interaction. In many cases of explosive molecules, the stronger the trigger bonds of explosive molecules, the greater the insensitivity [16]. Thus, it can be predicted that metal ion interaction reduces the sensitivity of the NTO molecule and NTO-Be²⁺ has the lowest sensitivity among the other metal ions.

From Figure 2, it can be seen that the distance O7-Li⁺ is 2.053 Å and O7-Na⁺ is 2.432 Å for B3LYP/6-31++G**.

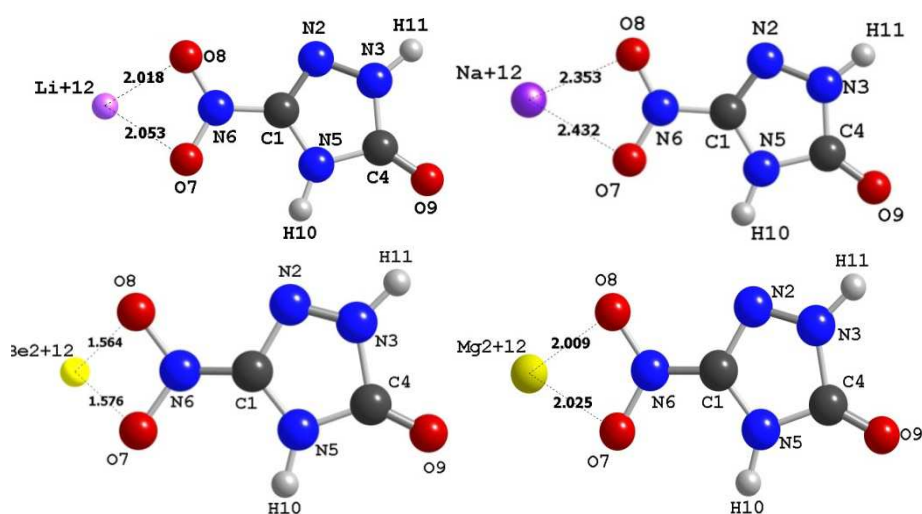


Figure 2. Optimized Structures of NTO-cations at B3LYP/6-31++G** Level of Theory

For comparison, in the molecule-cation complex Li⁺-(CH₃NO₂) and Na⁺-(paranitroaniline), the distance of O-Li⁺ and O-Na⁺ is 2.091 and 2.371 Å, respectively, using MP2(full)/6-31g++** [16].

Table 1. The Calculated Bond Length (in Å) and Experimental Bond Length of NTO Molecules

Bond length	B3LYP	Experiment
C(1)-N(2)	1.297	1.266
N(2)-N(3)	1.359	1.400
C(4)-N(5)	1.402	1.390
N(6)-O(7)	1.223	1.230
C(1)-N(5)	1.368	1.364
N(3)-C(4)	1.399	1.385
C(4)-O(9)	1.214	1.204
N(6)-O(8)	1.238	1.251
C(1)-N(6)	1.446	1.419
N(3)-H(11)	1.010	0.994
N(5)-H(10)	1.011	0.996

Table 2. The Calculated Bond Length of C1 and N6 nitro Group of NTO Complexes and Interaction metal-NTO

Bond Length	NTO	Li ⁺ -NTO	Na ⁺ -NTO	Be ²⁺ -NTO	Mg ²⁺ -NTO
C1-N6	1.497	1.435	1.442	1.331	1.341
N6-O7	1.205	1.225	1.235	1.340	1.320
N6-O8	1.215	1.248	1.227	1.330	1.320
M-O7	-	2.053	2.432	1.576	2.025

For the NTO analog (3,4-dinitropyrazole/DNP), the distance is 2.076 Å for DNP-Li⁺ and 2.438 Å for DNP-Na⁺ at MP2(full)/6-31g++**. This indicates that the current calculation is similar to the higher level of theory. The experimental values of O-Be and O-Mg in BeO and MgO are 1.331 and 1.749 Å [17]. Here, it is found that the distance O7-Be²⁺ is 1.576 Å and O7-Mg²⁺ is 2.025 Å, which are 0.25 – 0.50 Å longer than the distance in ionic compounds BeO and MgO. This indicates that interaction between the nitro functional group in NTO and metal ions might be significant. The order of interaction distance between nitro functional group in NTO and metal ions follows the order of NTO-Na⁺ > NTO-Li⁺ > NTO-Mg²⁺ > NTO-Be²⁺. From here, it can be predicted that the enhancement in interaction energies follows the order NTO-Be²⁺ < NTO-Mg²⁺ < NTO-Li⁺ < NTO-Na⁺.

Energies and sensitivities. The calculated interaction energies and BDE for NTO-metal ion complexes is shown in Table 3. It can be seen that the interaction energy follows the order NTO-Na⁺ < NTO-Li⁺ < NTO-Mg²⁺ < NTO-Be²⁺. It is consistent with the bond length analysis for each complex. The NTO-Li⁺ and NTO-Na⁺ complexes have smaller interaction energies (-156.95 kJ/mol dan -112.30 kJ/mol) than the NTO-Be²⁺ and NTO-Mg²⁺ corresponding complexes with -981.70 kJ/mol dan 541.77 kJ/mol, respectively. The interaction energies for alkali earth cation are stronger than those of alkali cation, which are very similar to the result obtained previously. For example, the complexes DNP-Li⁺, DNP-Na⁺ are -174.47 kJ/mol and -129.77 kJ/mol and DNP-Be²⁺ and DNP-Mg²⁺ are -963.43 kJ/mol and -544.41 kJ/mol, respectively, using B3LYP/6-311++G(2df,2p) [11].

The strength of the C1-N6 bond correlates with the decrease of the distance of the C1-N6 bond. Correlation between the C1-N6 bond and bond dissociation energies of C1-N6 is shown in Figure 3 at B3LYP/6-31++g**^{*}. The coefficient correlation is 0.93045 and its linear equation follows equation 3:

$$\text{BDE} = -5.507 \times 10^3 r + 8.129 \times 10^3 \quad (3)$$

The relationship between the bond dissociation energies of the C1-N6 bond in the NTO monomer and complexes with interaction energy B3LYP/6-31++g**^{*} is shown in Figure 4. It is clearly shown that B3LYP/6-31++g**^{*} produces linear correlation between BDE and interaction energy. The coefficient correlation up to 0.99899 for B3LYP/6-31++g**^{*} and its linear equation follows Equation 4:

$$\text{BDE} = -0.752E_{\text{int}} + 262.92 \quad (4)$$

Table 3 shows that the dissociation energy of C1-N6 in the NTO monomer from B3LYP/6-31++g**^{*} is 281.39 kJ/mol. This value is very close to experimental bond

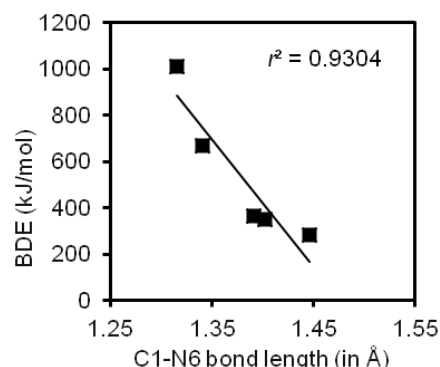


Figure 3. The C1-N6 Bond Dissociation Energy of the NTO Monomer and Complexes versus C1-N6 Bond Length at B3LYP/6-31++g**^{*} Level of Theory. The Correlation Coefficient is 0.9304

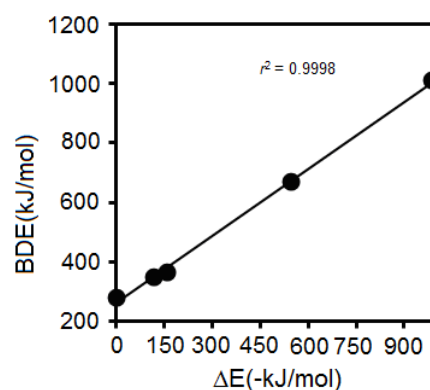


Figure 4. The C1-N6 Bond Dissociation Energy of Complexes versus Interaction Energy at B3LYP/6-31++G**^{*} Level of Theory. The Correlation Coefficient is 0.99899

dissociation energy C-N nitro group in 1,3-dinitrobenzene (278.10 kJ/mol) and 1,4-dinitrobenzene (280.19 kJ/mol) [16]. The bond dissociation energies for C1-N6 in complexes are greater than the NTO monomer. The strongest dissociation energy is found in NTO-Be²⁺ complex (1008.54 kJ/mol). This is three times higher than the bond dissociation energies of the NTO monomer (281.39 kJ/mol). The bond dissociation energies follow the order of NTO-Na⁺ < NTO-Li⁺ < NTO-Mg²⁺ < NTO-Be²⁺. These results show that the bond dissociation energies of C1-N6 are enhanced and the sensitivity is reduced after the formation of complexes.

Mulliken population analysis for NTO and each complex is shown in Table 4. The net charge of the nitro group after complexation tends to be more positive when compared with the NTO monomer as a result of electron distribution toward the positively charged metal cation. Mulliken population analysis gives charge transfer information from NTO toward each metal by 0.401, 0.213, 1.281, 0.677 for NTO-Li⁺, NTO-Na⁺, NTO-Be²⁺ and NTO-Mg²⁺, respectively. The greatest

charge transfer is obtained from NTO-Be²⁺ complex where it has the highest interaction energy of all NTO complexes. The result of the atomic charge analysis agrees with structural interaction energies and bond dissociation energy analysis.

The relationship between charge transfer with dissociation energy C1-N6 bond in complexes is shown in Figure 5. Coefficient correlation up to 0.9841 and its linear equation is shown in Equation 5.

$$\text{BDE} = 657.42Q \text{ Mulliken} + 174.550 \quad (5)$$

Analysis of electron density distribution. It is known that changes in the electron density distribution in both donors and acceptors are the most important consequence of the formation of the supramolecular interaction or non-

covalent interaction [18,19]. To visualize the nature of the supramolecular interaction of NTO with Li⁺, Na⁺, Be²⁺ and Mg²⁺, the shifts of electron density are calculated and illustrated in Figure 6. Red areas represent the accumulation of electron density; green areas indicate loss of density. As is shown in Figure 6, the Li⁺, Na⁺, Be²⁺ and Mg²⁺ ions are surrounded by much red area and the nitro group is surrounded by green area. It is suggested that the electron density of the nitro group has been lost toward cation and the supramolecular interaction has formed between NTO and Li⁺, Na⁺, Be²⁺ and Mg²⁺ ions. Moreover, the red area around the Li⁺, Na⁺, Be²⁺ and Mg²⁺ ions is the most significant in Be²⁺-NTO, indicating that the supramolecular interaction between Be²⁺ and NTO is the strongest.

Table 3. Interaction Energy (kJ/mol) and BDE (Bond Dissociation Energy (kJ/mol)) of the Complexes

Energy	NTO	Li ⁺ -NTO	Na ⁺ -NTO	Be ²⁺ -NTO	Mg ²⁺ -NTO
ΔE	-	- 159.1	- 115.46	- 984.82	- 544.76
E _{BSSE}	-	-	-	-	-
ΔE _{BSSE}	-	- 156.9	- 112.30	- 981.70	- 541.77
BDE C1-N6	281.39	365.6	348.79	1008.54	668.45

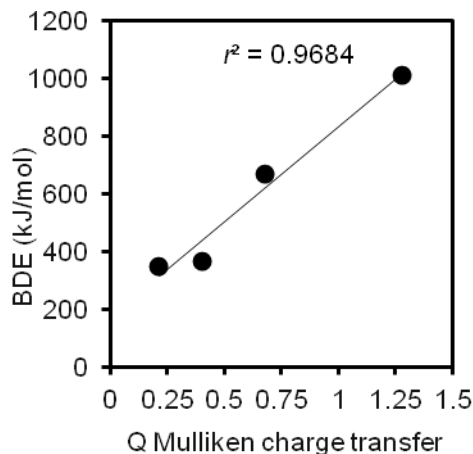


Figure 5. The C1-N6 Bond Dissociation Energy of Complexes versus Charge Transfer Cation-NTO at B3LYP/6-31++g Level of Theory. Coefficient Correlation up to 0.9684**

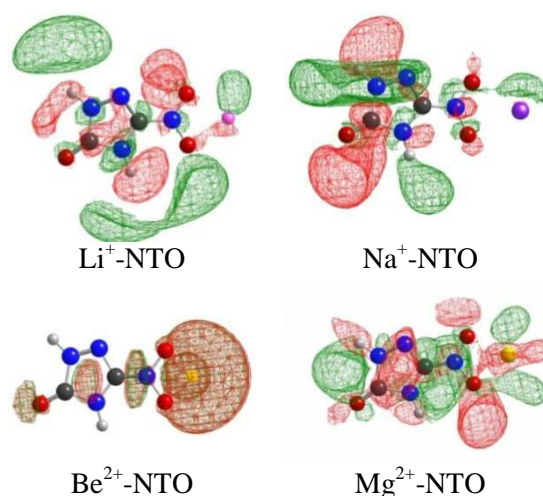


Figure 6. Distribution of Electron Density as a Result of Formation of the Complex between NTO and Li⁺, Na⁺, Be²⁺, Mg²⁺ at B3LYP/6-31++g level of theory. Red Regions Denote Gain, and Green Regions Represent Loss**

Table 4. Mulliken Atomic Charge of the NTO Monomer and Each Complex at B3LYP/6-31++G Level of Theory**

Parameter	NTO	Li ⁺ -NTO	Na ⁺ -NTO	Be ²⁺ -NTO	Mg ²⁺ -NTO
N(6)O(7)O(8)	-0.184	-0.08	-0.204	0.151	-0.213
M	-	0.599	0.787	0.719	1.323
Charge transfer	-	0.401	0.213	1.281	0.677

It is interesting that there is much red area around the C1–N6 bond, showing that the electron density also shifts from the nitro group toward the C1–N6. It is well known that the more intensive an electron cloud between two atoms, the more chances for overlapping. As a result, the strength of the C1–N6 bond is increased.

As can be seen in Figure 6, the red area around the C1–N6 bond of NTO-Be²⁺ is the most significant, suggesting that the C1–N6 bond in NTO- Be²⁺ is the strongest and has the lowest sensitivity, as it is well correlated with bond length and bond dissociation energy of the C1–N6 bond. Thus, it can be concluded that upon the formation of the supramolecular interaction between NTO and metal ions, the strength of the C1–N6 bond is enhanced and the sensitivity of the explosive NTO is reduced.

Conclusions

The explosive sensitivity of high energetic material, 3-nitro-1,2,4-triazol-5-one (NTO), in intermolecular interaction with metal ions (Li⁺, Na⁺, Be²⁺ and Mg²⁺) was studied using DFT at B3LYP/6-31++g** level of theory. The longest bond length of the NTO molecule is from the C1–N6 bond and considered as the trigger bond. After the interaction of NTO and metal ions occurred, the C1–N6 bond length decreased so that the sensitivity of the explosive was also reduced. The enhancement interaction energy and BDE of C1–N6 follows the order of NTO-Na⁺ < NTO-Li⁺ < NTO-Mg²⁺ < NTO-Be²⁺. The enhancement of the trigger bond dissociation energy in comparison with the NTO monomer correlated well with the complex interaction energies and Mulliken charge transfer. Thus, the presence of metal ions (Li⁺, Na⁺, Be²⁺ and Mg²⁺) strengthened the trigger bond so that the sensitivity of NTO was reduced.

Acknowledgements

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