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Jichuan Zhang, Hui Su, shu guo, yalu dong, Shaowen Zhang, tao zou, Shenghua Li, and Siping Pang

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Fine-Tuning the Energetic Properties of Complexes through Ligand Modification

Ji-Chuan Zhang,[†] Hui Su,[†] Shu Guo,[§] Ya-Lu Dong,[†] Shao-Wen Zhang,[‡] Tao Zou,[§] Sheng-Hua Li,^{*,†} and Si-Ping Pang^{*,†}

[†]School of Materials Science & Engineering, Beijing Institute of Technology, South Street No.5, Zhongguancun, Haidian District, Beijing 100081, PR, China

[‡]School of Chemistry, Beijing Institute of Technology, South Street No.5, Zhongguancun, Haidian District, Beijing 100081, PR, China,

[§]Beijing Center for Physical and Chemical Analysis, Xisanhuanbeilu No.27, Haidian District, Beijing, 100089, PR, China.

KEYWORDS: Energetic Materials; Energetic Properties; Modulation; Groups; Modification

ABSTRACT. The modification of the properties of energetic materials is significant not only for gaining insight into the correlation between the structure and properties but also for various applications. In this study, three bis-1,2,4-triazole derivatives containing different energetic groups such as NH₂, NO₂, and NHNO₂ [5,5'-diammino-3,3'-bis-1,2,4-triazole (H₂DABT), 5,5'-dinitro-3,3'-bis-1,2,4-triazole (H₂DNBT) and 5,5'-dinitroimino-3,3'-bis-1,2,4-triazole (H₂DNABT)], were chosen as ligands to tune the structures and energetic properties of their complexes. The single crystal X-ray diffraction show that as the modifying groups on the bis-1,2,4-triazole ligand were varied from NH₂, NO₂ to NHNO₂, the densities of the resultant complexes gradually increased from 1.838 g cm⁻³, 1.978 g cm⁻³ to 2.049 g cm⁻³ for Cu-based complexes, while for Zn-based complexes, the densities also showed a gradual increase from

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3 1.818 g cm⁻³, 2.044 g cm⁻³ to 2.056 g cm⁻³. Additionally, the thermal stabilities and sensitivities
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5 of these complexes were also determined, and their detonation properties were calculated by the
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7 modified Kamlet's method. As a result, the energetic performances of these resultant complexes
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9 were successfully modulated. This work may provide an effective approach to modulate the
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11 energetic properties of complexes via introduction of different energetic groups into the ligands.
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16 17 INTRODUCTION

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19 Modulation of properties (e.g., density, thermal stability, sensitivity, heat of detonation,
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21 detonation velocity and detonation pressure) of energetic materials have attracted growing
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23 attention not only for gaining insight into the correlation between the structure and properties but
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25 also for various applications such as explosives,¹⁻⁵ propellants,⁶⁻⁹ pyrotechnics,¹⁰⁻¹⁶ carbon
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27 nitride precursors and their energetic analogous,¹⁷⁻¹⁹ and gas-generating agents.²⁰⁻²¹ For example,
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29 gas-generating agents should ideally produce more gas and less heat when used for air bags,
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31 primary explosives should be sensitive enough to be initiated, whereas secondary explosives
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33 should possess considerably higher detonation heat and lower sensitivities. Over the past decade,
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35 a variety of protocols for tuning the properties of energetic materials have been developed.²²⁻²⁵
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37 Among them, the introduction of different energetic groups (e.g., nitro,¹⁰⁻¹² nitroamine,^{13, 14}
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39 azido,¹⁶ and amino¹⁷) as substituents on an organic backbone is perhaps the most commonly used
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41 method for this purpose. For instance, the introduction of a nitro group improves the oxygen
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43 balance and density, and thus the detonation properties of energetic materials,²⁶ whereas the
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45 introduction of an amino group enhances the stability and reduces sensitivity.²⁷ To date, this
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47 method is primarily used for energetic organic molecules or energetic salts. In contrast,
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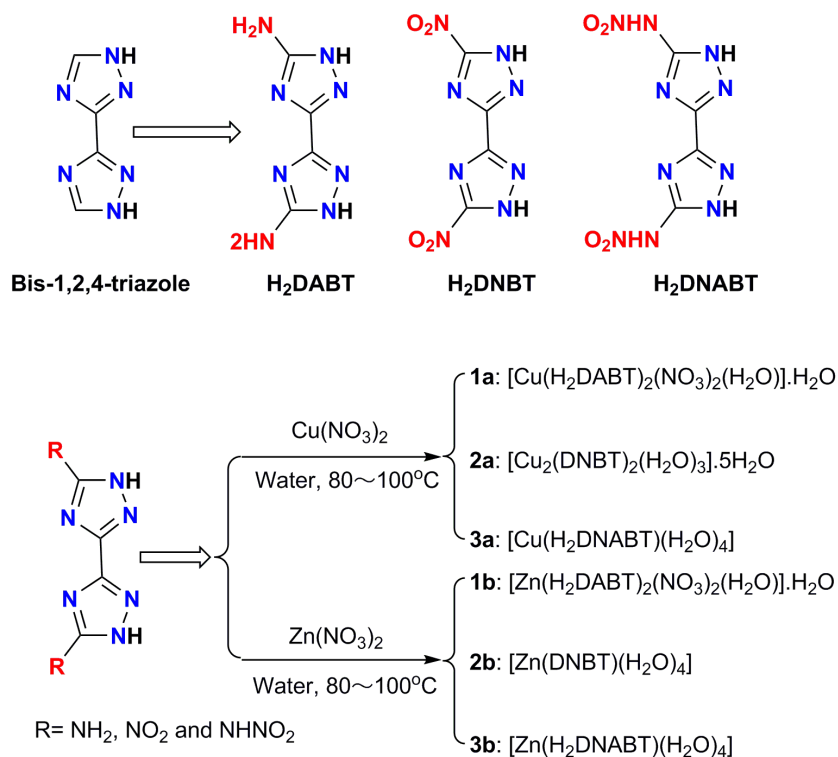
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3 employing this method to tune the properties of energetic complexes and energetic metal-organic
4 frameworks has scarcely reported.²⁸
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8 Energetic complexes are an important class of energetic materials, which possess high
9 densities and high thermal stabilities. These materials have exhibited promising applications as
10 pyrotechnics and primary explosives,^{29–38} and have been constructed exclusively with strong
11 coordination bonds between nitrogen-rich ligands and metal ions. Till now, their structures and
12 properties are primarily different owing to various of metal ions and organic ligands with
13 different backbones.^{39–47} However, the modulation of their energetic properties via introduction
14 different energetic groups on a same backbone (ligand) has been rarely reported. The proposed
15 modulation also facilitates exploring the effects of energetic groups on the structures and
16 properties of energetic complexes, which are important for better designing new high-
17 performance energetic materials.
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31 As an important energetic backbone, bis-1,2,4-triazole possesses a high nitrogen content
32 (N%= 61.74) and a high heat of formation. It has a few carbon atoms in the azole ring, which
33 facilitates introducing different energetic groups into the backbone. Moreover, it contains more
34 than six potentially coordinated N atoms in a molecule. We envisage that these features could
35 make it as an ideal energetic ligand for the development of energetic complexes and tuning their
36 properties. Hence, we reported the synthesis of a series of energetic complexes employing bis-
37 1,2,4-triazole derivatives containing different energetic groups such as NH₂, NO₂ and NHNO₂
38 (H₂DABT: 5,5'-diamino-3,3'-bis-1,2,4-triazole; H₂DNBT: 5,5'-dinitro-3,3'-bis-1,2,4-triazole and
39 H₂DNABT: 5,5'-dinitroimino-3,3'-bis-1,2,4-triazole, **Scheme 1**) as ligands,⁴⁸ and Cu²⁺ and Zn²⁺
40 as central metal ions, respectively. The effect of energetic groups on the structures and properties
41 of these energetic complexes were investigated. The results showed that the energetic properties
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of resultant complexes may be conveniently tuned via varying the energetic groups of ligands from NH_2 , NO_2 to NHNO_2 .

Scheme 1. Synthesis of six energetic complexes based on H_2DABT , H_2DNBT , and H_2DNABT ligands.



EXPERIMENTAL SECTION

Safety Precautions. Although none of the energetic complexes described herein exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices

General Methods. H_2DABT , H_2DNBT , and H_2DNABT were prepared according to the literature.⁴⁸ All other materials were commercially available and used without further purification.

IR spectra were recorded on a Bruker Tensor 27 spectrophotometer with a high-throughput extension (HTS-XT) accessory (KBr pellets). Elemental analysis was performed on an Elementar

Vario EL instrument (Germany). To determine the thermal stabilities of the as-synthesized energetic complexes, a TG-DSC Q2000 differential scanning calorimeter was used (heating rate: 5 °C min⁻¹; flow rate of nitrogen gas: 60 mL min⁻¹; sample size: approximately 1.0 mg). The densities of the energetic complexes were measured using an automatic density analyzer (ULTRAPYC 1200e.)

X-ray Crystallography. The crystal structures of the energetic complexes were determined using a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoK α radiation source ($\lambda = 0.71073 \text{ \AA}$) and the SHELXTL software package for crystallographic molecular structure. Single crystals were mounted on the diffractometer, and data were collected by the ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined by theoretical calculations and refined with an isotropic vibration factor.

Synthesis of Cu(H₂DABT)₂(NO₃)₂(H₂O)] H₂O (1a). A solution of Cu(NO₃)₂ · 3H₂O (3.6 g, 15 mmol) in water (5 ml) was added to a solution of H₂DABT (0.85 g, 5 mmol) in 150 ml boiling water, stirred for 5 min at 100 °C, and then the resulting solution was filtered. Green needle-like crystals were obtained by slow evaporation at room temperature in a glass vial within 2 days. Yield: 68% based on H₂DABT. Calcd for C₈H₁₆CuN₁₈O₈ (M = 555.9 g mol⁻¹): C 17.27, H 2.88, N 45.33; found C 17.40, H 2.48, N 45.86. Main IR (KBr, cm⁻¹): 3594 (m), 3413 (s), 3343 (m), 3112 (m), 1660 (s), 1636 (s), 1473 (m), 1361 (s), 1275 (m), 1112 (m), 823 (w), 776 (m), 478 (w).

Synthesis of Zn(H₂DABT)₂(NO₃)₂(H₂O)] H₂O (1b). A mixture of Zn(NO₃)₂ · 6H₂O (4.55 g, 15 mmol) and H₂DABT (0.83 g, 5 mmol) in water (150 mL) was stirred for 2 h at 80 °C and then the resulting solution was filtered. Colourless transparent crystals were obtained by slow

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3 evaporation at room temperature in a glass vial within 2 days. Yield: 66% based on H₂DABT.

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5 Anal.calcd for C₈H₁₆N₁₈O₈Zn (M= 557.7 g mol⁻¹): C 17.21, H 2.87, N 45.19; found C 17.38, H
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7 2.42, N 45.80. Main IR (KBr, cm⁻¹): 3592 (w), 3529 (w), 3417 (m), 3338 (m), 3241 (m), 3185
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9 (m), 3132 (m), 3007 (m), 2869 (m), 2810 (m), 1657 (s), 1474 (s), 1111 (m), 1073 (m), 1051 (w),
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11 979 (w), 823 (w), 777 (w), 731 (w).

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14 **Synthesis of [Cu₂(DNBT)₂(H₂O)₃] 5H₂O (2a).** A solution of Cu(NO₃)₂ 3H₂O (2.41 g, 10 mmol)
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16 in water (5 ml) was added slowly to a solution of H₂DNBT 2H₂O (1.31 g, 5 mmol) in water (100
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18 ml), maintained at 80 °C for 8 h without stirring, and then allowed to cool slowly to room
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20 temperature. Blue needle-like crystals were obtained. Yield: 57% based on H₂DNBT. Anal.calcd
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22 for C₈H₁₆N₁₆O₁₆Cu₂ (719.5 g mol⁻¹): C 13.34, H 2.22, N 31.13; found C 13.28, H 2.08, N 31.33.
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24 Main IR (KBr, cm⁻¹): 3594 (m), 3558 (m), 3356 (m), 1612 (m), 1544 (s), 1443 (s), 1403 (s),
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26 1367 (m), 1335 (w), 1308 (s), 1193 (m), 1171 (w), 1098 (w), 1011 (w), 840 (s), 710 (m), 658 (m).
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31 **Synthesis of [Zn(DNBT)(H₂O)₄] (2b).** A solution of Zn(NO₃)₂ 6H₂O (4.45 g, 15 mmol) in
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33 water (5 ml) was added slowly to a solution of H₂DNBT 2H₂O (1.31 g, 5 mmol) in water (100
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35 ml), maintained at 90 °C for 6 h, and then allowed to cool slowly to room temperature. Yellow
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37 crystals were obtained. Yield: 63% based on H₂DNBT. Anal.calcd for C₄H₈N₈O₈Zn (361.5 g
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39 mol⁻¹): C 13.28, H 2.21, N 30.98; found C 12.98, H 2.26, N 30.55. Main IR (KBr, cm⁻¹): 3440
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41 (m), 1668 (w), 1531 (s), 1506 (m), 1451 (s), 1408 (m), 1363 (m), 1345 (m), 1297 (s), 1243 (m),
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43 1183 (w), 1105 (m), 1020 (w), 1007 (w), 838 (m), 718 (m).
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47 **Synthesis of [Cu(H₂DNABT)(H₂O)₄] (3a).** A solution of Zn(NO₃)₂ 6H₂O (2.17 g, 9 mmol) in
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49 water (5 ml) was added slowly to a solution of H₂DNABT 2H₂O (0.8 g, 1 mmol) in 5% dilute
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51 nitric acid (100 ml), maintained at 80 °C for 6 h, and then allowed to cool slowly to room
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53 temperature. Blue crystals were obtained. Yield: 61% based on H₂DNABT. Anal.calcd for
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3 $C_4H_{10}N_{10}O_8Cu$ (389.8 g mol⁻¹): C 12.31, H 2.57, N 35.92; found C 12.03, H 2.63, N 35.48. Main
4
5 IR (KBr, cm⁻¹): 3457 (m), 3429 (m), 3111 (m), 1666 (w), 1561 (m), 1518 (m), 1453 (m), 1407
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7 (w), 1341 (s), 1300 (m), 1280 (s), 1261 (m), 1114 (m), 1020 (m), 812 (w), 778 (w), 739 (m), 498
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9 (w).

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12 **Synthesis of [Zn(H₂DNABT)(H₂O)₄] (3b).** A solution of Zn(NO₃)₂ · 6H₂O (2.67 g, 9 mmol) in
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14 water (5 ml) was added slowly to a solution of H₂DNABT · 2H₂O (0.8 g, 1 mmol) in water (100
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16 ml), maintained at 90 °C for 8h, and then allowed to cool slowly to room temperature. Yellow
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18 crystals were obtained. Yield: 60% based on H₂DNABT. Anal.calcd for C₄H₁₀N₁₀O₈Zn (391.6 g
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20 mol⁻¹): C 12.26, H 2.55, N 35.75; found C 12.05, H 2.63, N 35.11. Main IR (KBr, cm⁻¹): 3316
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22 (m), 1612 (m), 1552 (m), 1505 (m), 1447 (w), 1344 (s), 1293 (s), 1242 (m), 1104 (m), 1056 (w),
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24 1020 (m), 987 (w), 863 (w), 796 (w), 726 (w), 655 (w).

30 RESULTS and DISCUSSION

31 X-ray crystallography

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35 Complexes **1a** and **1b** are extremely similar in structure as both of them crystallized in the
36
37 triclinic *P*-1 space group. The asymmetric unit contains two H₂DABT molecules, one metal
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39 cation (Cu^{II} or Zn^{II}), two NO₃⁻ anions, one coordinated water molecule, and one crystal water
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41 molecule. As shown in **Figure 1-2**, **S5**, and **S6**, the central Cu or Zn is five-coordinated with four
42
43 nitrogen atoms from the two H₂DABTs and one oxygen atom from the coordinated water,
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45 forming a distorted square pyramid, The torsional angle between the two DABT molecules in **1a**
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47 is 44.54 °, while that in **1b** is 43.63 °. The formation of the torsional angles could result from the
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49 mutual repulsion between the two amino groups from the opposite DABTs. The lengths of Cu–N
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51 bonds in **1a** are approximately 2.000 Å, which are slightly shorter than those of Zn–N bonds in
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53 **1b** (e.g., Cu1-N1= 1.9704 Å; Cu1-N5'= 1.9674 Å; Zn1-N1= 2.0635 Å, Zn1-N5'= 2.00325 Å),
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possibly because Zn has a slightly larger radius than Cu. To explore the coordination abilities of all nitrogen atoms in H₂DABT, B3LYP/6-311+G^{**} level was employed to calculate the charge densities of the nitrogen atoms. The results demonstrated that the charge densities of N1 and N5 reach up to -0.580 and -0.583 respectively, which are remarkably lower than those of other nitrogen atoms (e.g., N2, -0.337; N6, -0.335, Figure S1). Thus, N1 and N5 possess stronger coordination stabilities, and form coordination bonds with metal ions with a relatively more ease, which is confirmed from the crystal structures of **1a** and **1b**. Moreover, in **1a** and **1b**, the NO₃⁻ anions, and the amino groups from the H₂DABT participate in the N-H...O hydrogen bonding, where the lengths of the hydrogen bonds range from 2.8132 to 3.1594 Å. The crystal parameters and the selected bond lengths and angles are listed in Tables S2 and S3.

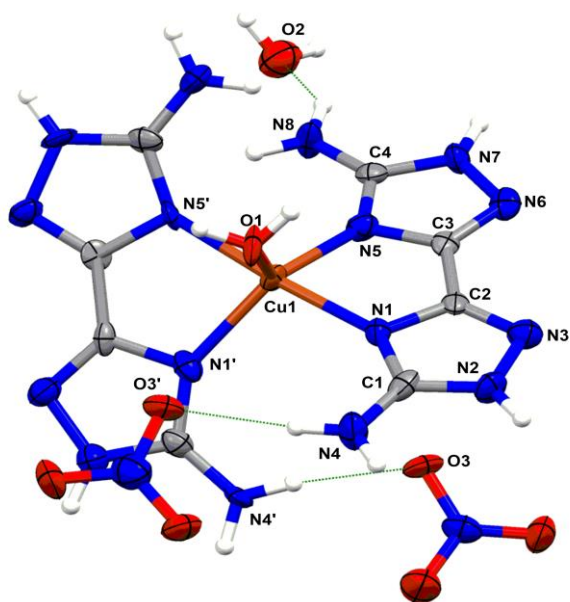


Figure 1. Crystal structure of **1a** and its labeling scheme. Ellipsoids are drawn at 50% probabilities. Hydrogen atoms are shown as spheres of arbitrary radius. Hydrogen bonds are marked by dotted lines.

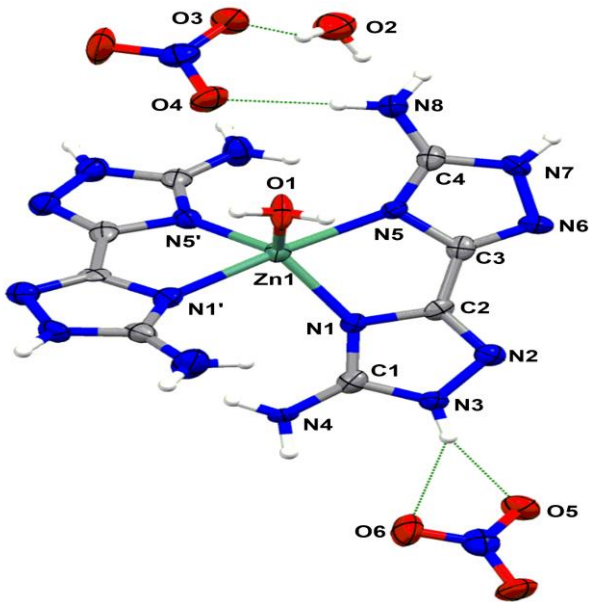


Figure 2. Crystal structure of **1b** and its labeling scheme. Ellipsoids are drawn at 50% probabilities. Hydrogen atoms are shown as spheres of arbitrary radius. Hydrogen bonds are marked by dotted lines.

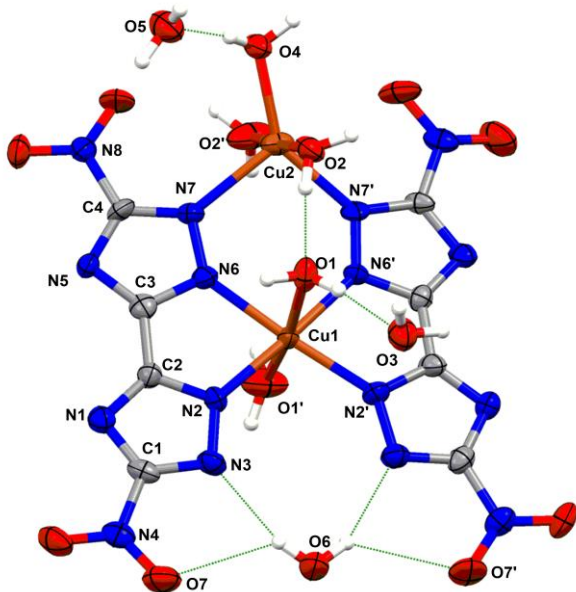


Figure 3. Crystal structure of **2a** and its labeling scheme. Ellipsoids are drawn at 50% probabilities. Hydrogen atoms are shown as spheres of arbitrary radius. Hydrogen bonds are marked by dotted lines.

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5 The structure of complex **2a** is distinctly different from that of **1a** as it crystallized in the
6 orthorhombic $Pna2_1$ space group and its asymmetry unit contains two DNBT^{2-} ions, two Cu^{2+}
7 ions, four coordinated water molecules, and four crystal water molecules. As shown from **Figure**
8 **3**, the central copper ion ($\text{Cu}^{\text{II}1}$) is hexa-coordinated with four nitrogen atoms from two
9 symmetrical DNBT^{2-} anions and two oxygen atoms from coordinated water molecules.
10 Furthermore, another copper ion ($\text{Cu}^{\text{II}2}$) ion is penta-coordinated with two nitrogen atoms from
11 two DNBT^{2-} ions and three oxygen atoms from coordinated water molecules. Although the
12 results of NBO calculation shows that the nitrogen atoms that possess the maximum charge
13 values, are N1 (-0.529) and N5 (-0.531) (Figure S2), Cu (1) is actually coordinated with N2 and
14 N6. This may be due to that the size of a nitro group in the DNBT ligand is larger than the amino
15 group in the H_2DABT ligand; if Cu (1) is coordinated with N1 and N5, the mutual repulsion
16 between the two nitro groups from the opposite DNBT ligands could make the structure unstable.
17 Additionally, the lengths of Cu1-N bonds are slightly longer than those of Cu2-N bonds. For
18 example, the bond lengths of Cu1–N2 and Cu1–N6' are 1.9983 and 2.0048 Å, respectively, while
19 those of Cu2–N7 and Cu2–N7' are 2.1964 and 2.0631 Å, respectively. In addition, free water
20 molecules and nitro groups of DNBT^{2-} ions also participate in the N–H•••O hydrogen bonding,
21 where the lengths of the hydrogen bonds are about 2.6863 Å.
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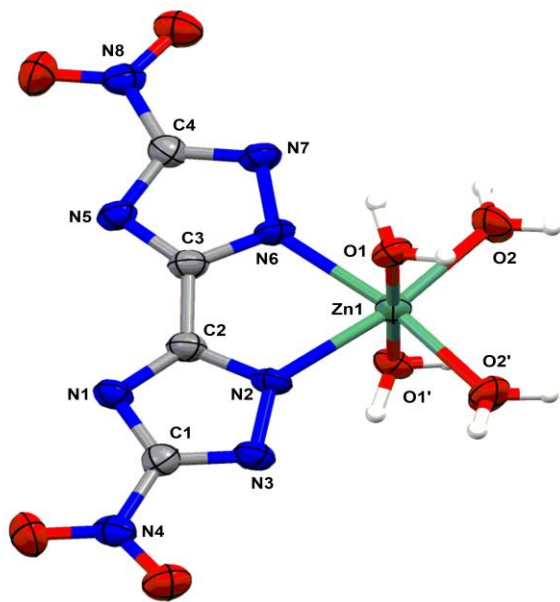
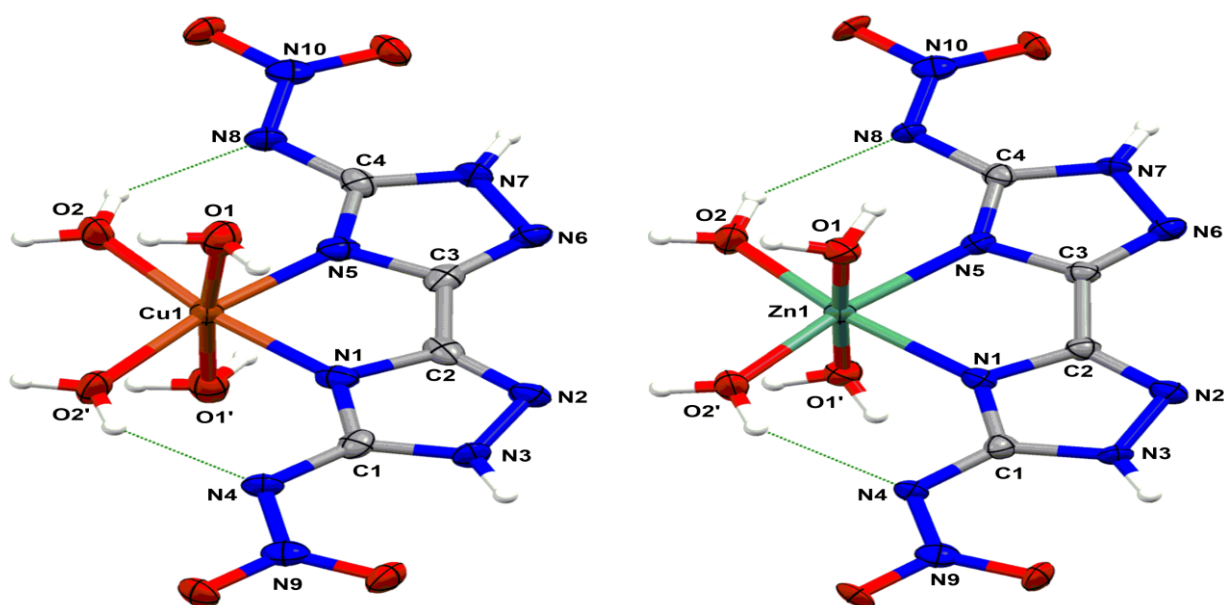


Figure 4. Crystal structure of **2b** and its labeling scheme. Ellipsoids are drawn at 50% probabilities. Hydrogen atoms are shown as spheres of arbitrary radius. Hydrogen bonds are marked by dotted lines.

Complex **2b** crystallized in the monoclinic $c2/c$ space group with one DNBT^{2-} anion, one Zn^{II} cation, and four coordinated water molecules per unit. As shown in **Figure 4**, the central Zn^{II} is hexa-coordinated with two nitrogen atoms from one DNBT^{2-} ion and four oxygen atoms from four coordinated water molecules, forming a regular octahedron. Interestingly, the structure of **2b** is clearly different from that of **2a**; **2b** appears to be about half the size of **2a**, possibly because (1) Zn^{2+} has a larger radius than Cu^{2+} , as if Zn lies at the site of Cu1 in structure **2a**, the distance between the two DNBT^{2-} ions could become longer, making the structure unstable; (2) the coordinated nitrogen atom N6 has a lower charge density than N7 (N7, -0.339; N6, -0.347). If the Cu2 site is replaced by Zn2, the larger distance between the two symmetrical DNBT^{2-} ions could not offer the coordination environment for Zn2 and N7 (N7'). To verify the proposed hypothesis, cam-b3lyp/cep-121G was employed to analyze and calculate the free energy of

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3 structures **2b** and **2a'**, in which Zn^{2+} replaces Cu^{2+} in structure **2a**. The results show that the
4 structure of **2b** has a lower free energy ($16.8 \text{ kcal mol}^{-1}$) than that of structure **2a'** (Figure S4);
5
6 therefore, **2b** has a higher stability than that of **2a'**. Because the two coordinated water and Zn
7 are located in a straight line, the O1-Zn1-O1' acts as a pillar and is vertical to the plane of
8 DNBT²⁻ ions. Meanwhile, multi-hydrogen bonds are formed between the hydrogen atoms from
9 the water molecules and the O atoms from the nitro groups, leading to the 3D network structure
10 in **2b** (Figure S8).



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Figure 5. Crystal structures of **3a** (left) and **3b** (right). Ellipsoids are drawn at 50% probabilities. Hydrogen atoms are shown as spheres of arbitrary radius. Hydrogen bonds are marked by dotted lines.

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The crystal structures of **3a** and **3b** (Figure 5) are also similar as both of them crystallized in the monoclinic $c2/c$ space group with one DNABT²⁻ ion, one Cu^{2+} or Zn^{2+} ion, and four coordinated water molecules per unit. As shown in Figure 5, the central copper or zinc is hexacoordinated with two nitrogen atoms from one DNABT ion and four oxygen atoms from four coordinated waters, forming an octahedron. The NBO calculation results show that N1 and N5

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3 have lower charge densities (-0.554) than those of other nitrogen atoms in DNABT (Figure S3),
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5 implying that N1 and N5 are the most likely sites to coordinate to metal ions, which is in
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7 agreement with the coordination modes for **3a** and **3b**. The formed hydrogen bonds are
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9 symmetrical between deprotonated N8 (N4) and O2 (O2'); in the similar way with crystal **2b**, the
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11 3D hydrogen bonds network resides in **3a** and **3b** (Figure S9 and S10).
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14 **Thermal stabilities**

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17 Differential scanning calorimetry (DSC)-thermogravimetric analysis (TG) measurements
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19 were performed at the heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to determine the dehydration temperatures and
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21 decomposition temperatures of energetic complexes (approximately 1.0 mg samples) (**Figure 6**).
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23 The onset decomposition temperatures of energetic complexes are given as their decomposition
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25 temperatures, whereas the dehydration temperatures are set at the minimum of the endothermic
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27 peaks in the DSC curve. For complexes **1a** and **1b**, the decomposition temperatures are $270\text{ }^{\circ}\text{C}$
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29 and $308\text{ }^{\circ}\text{C}$, while the decomposition temperatures of complexes **2a** and **2b** are $326\text{ }^{\circ}\text{C}$ and
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31 $315\text{ }^{\circ}\text{C}$, respectively. Complexes **3a** and **3b** decompose almost at the same temperature, are
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33 $187\text{ }^{\circ}\text{C}$ and $186\text{ }^{\circ}\text{C}$, respectively. Except for complex **3a**, all the complexes show endothermic
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35 peaks between $69\text{ }^{\circ}\text{C}$ and $132\text{ }^{\circ}\text{C}$, corresponding to the loss of water molecules.
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40 According to Kamlet-Jacobs equations,^{49,50} the detonation velocity (D) of an energetic
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42 material is proportional to its density and its detonation pressure (P) is proportional to the square
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44 of its density. Hence, density is one of most vital physical properties affecting the detonation
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46 performances of energetic materials. The densities of as-synthesized energetic complexes and
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48 their ligands were measured using an automatic gas pycnometer. As showed in **Figure 7**, the
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50 densities of DABT, DNBT, and DNABT are 1.60 , 1.90 , and 1.80 g cm^{-3} , respectively. For **1a**, **2a**,
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52 and **3a** based on Cu complexes, their densities are 1.838 , 1.978 and 2.049 g cm^{-3} . Therefore, as
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the modified groups were varied from NH_2 , NO_2 to NHNO_2 , the densities of resultant complexes improved gradually. Meanwhile, for **1b**, **2b**, and **3b** based on Zn complexes, their densities also exhibited a similar trend.

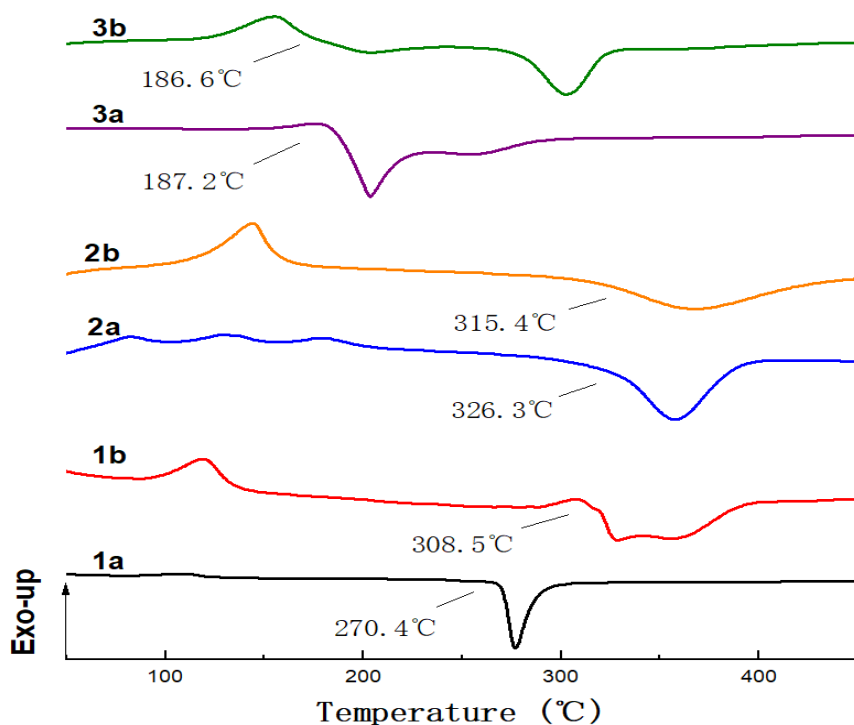


Figure 6. DSC curves of energetic complexes **1a-3a** and **1b-3b**

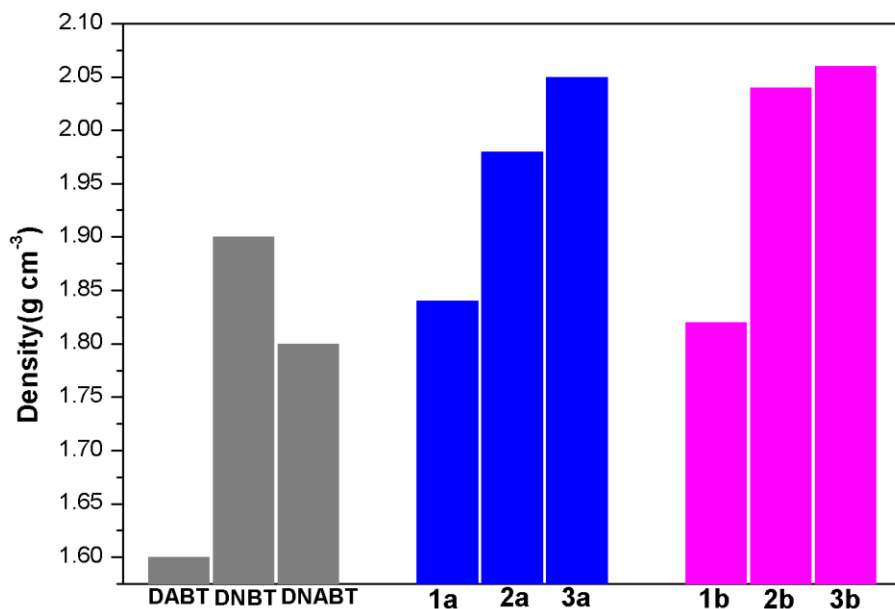


Figure 7. Densities of ligands and energetic complexes **1a-3a** and **1b-3b**

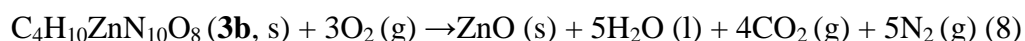
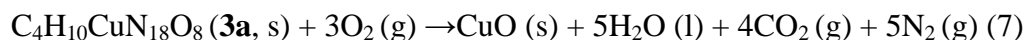
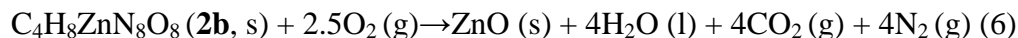
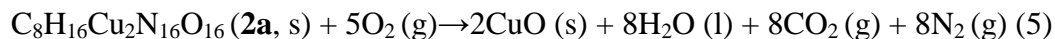
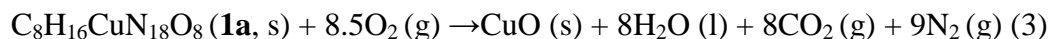
Energetic properties.

The heats of combustion and heats of formation are also two significant characteristics for assessing the energetic properties. The constant-volume combustion energies ($\Delta_c U$) for energetic complexes were measured by an oxygen bomb calorimeter; the values of $\Delta_c U$ were reported as the averages of three independent measurements. The enthalpy of combustion ($\Delta_c H^\theta$) was calculated from $\Delta_c U$ and a correction for change in gas volume during combustion was included (eq 1). The standard enthalpies of formation ($\Delta_f H^\theta$) were back calculated from the heats of combustion on the basis of combustion equations (eq 3-8), Hess's Law as applied in thermochemical equation (eq 2), and known standard heats of formation for copper oxide, water and carbon dioxide [CO_2 (g): $-393.51 \text{ kJ mol}^{-1}$; H_2O (l): $-285.83 \text{ kJ mol}^{-1}$; CuO (s): $-156.06 \text{ kJ mol}^{-1}$; ZnO (s): $-350.46 \text{ kJ mol}^{-1}$]⁵¹. The heats of formation for complexes **1a-3a** and **1b-3b** are -589, -789, -1719, -925, -812, and -973 kJ mol^{-1} , respectively.

$$\Delta_c H_m^\theta = Q_p = Q_v + \Delta n_g RT \quad (1)$$

where Δn_g is the variation in the number of gas constituents in the reaction process, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298.15 \text{ K}$.

$$\Delta_f H_m^\theta (\text{reactant, s}) = n\Delta_f H_m^\theta (\text{product 1, s}) + n\Delta_f H_m^\theta (\text{product 2, l}) + n\Delta_f H_m^\theta (\text{product 3, g}) - \Delta_c H_m^\theta (\text{reactant, s}) \quad (2)$$



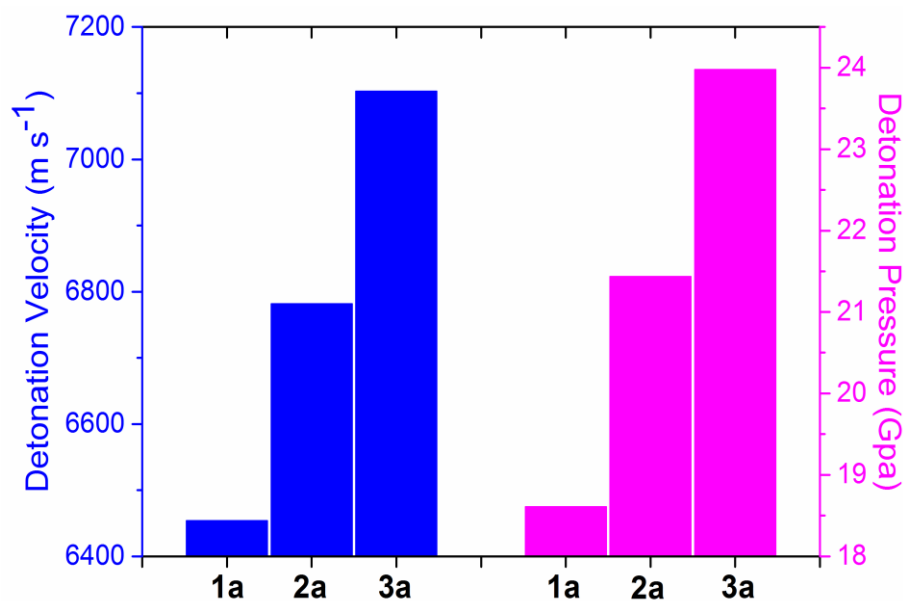


Figure 8. Variation trend of detonation velocities and pressures for **1a**, **2a**, and **3a**.

The detonation velocity (D) and detonation pressure (P) are commonly employed to estimate the power of explosives. To calculate the detonation velocities and detonation pressures of as-synthesized energetic complexes, we adopted our developed method based on Kamlet's method (Figure S12), that has widely been used to predict the detonation velocities and pressures of many energetic complexes.⁵² The results showed that the detonation velocities of **1a**, **2a**, and **3a** are 6454, 6782, 7103 ms^{-1} , while their detonation pressures are 18.61, 21.44, 23.98 GPa, respectively. Notably, the detonation performance of **3a** even exceeds TNT ($D= 6881 \text{ms}^{-1}$, and $P= 19.5 \text{GPa}$). As the substitute groups on bis-1,2,4-triazole ligands were varied from NH_2 , NO_2 to NHNO_2 , the detonation properties of their energetic complexes based on Cu ions (**1a-3a**) improved gradually (**Figure 8**); meanwhile, their velocities and pressures also successfully tuned. The detonation properties of energetic complexes based on Zn ions also exhibited the same trend as those based on Cu ions (Figure S13).

Table 1. Physicochemical Properties of Various Energetic Complexes and TNT.

	1a	1b	2a	2b	3a	3b	TNTⁿ
M^a	555.9	557.7	719.5	361.6	389.8	391.6	227
N^b	45.33	45.19	31.13	30.97	35.92	35.75	18.50
Ω^c	-48.9	-48.8	-22.2	-22.1	-24.6	-24.5	-74
T_d^d	270	308	326	315	187	186	295
ρ^e	1.838	1.818	1.978	2.044	2.049	2.056	1.65
$-\Delta_c U^f$	8941	8901	5546	5870	5993	6025	--
$-\Delta_f H^{\theta g}$	589	789	1719	925	812	973	59.4
D^h	6454	6137	6782	6839	7103	6873	6881
	(6846) ^m		(6712) ^m		(7220) ^m		
P^i	18.61	16.72	21.44	22.20	23.98	22.49	19.5
	(17.86) ^m		(19.48) ^m		(22.59) ^m		
IS^j	>40	>40	>40	>40	17	28	15
FS^k	>360	>360	360	>360	298	307	353
EDS^l	>44	>44	35.64	39.71	31.79	15.84	--

^amolecular mass (g mol⁻¹). ^bNitrogen content (%). ^cOxygen balance (%). ^dThe onset decomposition temperature (DSC, °C). ^eDensity calculated from their crystal densities according to reference 55 (g cm⁻³). ^fExperimental determined (oxygen bomb calorimetry) constant volume energy of combustion (kJ kg⁻¹). ^gExperiment determined (back-calculated from $-\Delta_c U$) enthalpy of formation (kJ mol⁻¹). ^hDetonation velocity were calculated by EXPLO5 v6.01. ⁱDetonation pressure were calculated by EXPLO5 v6.01. ^jImpact sensitivity (J). ^kFriction sensitivity (N). ^lElectrostatic sensitivity (J). ^mThe detonation properties were calculated by our developed method. ⁿReference 53.

For the initial safety testing, the impact (IS) and friction sensitivities (FS) of these energetic complexes were tested according to the Bundesamt für Materialforschung (BAM) standard method. As showed from Table 1, their impact sensitivities of complexes **1a**, **1b**, **2a**, and **2b** are higher than 40 J, while their friction sensitivities are higher than 360 N. According to the UN

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3 Recommendations on the Transport of Dangerous Goods,⁵⁴ these complexes are insensitive to
4 impact and friction. However, the impact and friction sensitivities of **3a** and **3b** are smaller than
5 40 J and 360 N (**3a**, IS= 17 J, FS= 298N; **3b**, IS= 28 J, FS= 307 N), and thus they are sensitive.
6
7 Additionally, the electrostatic sensitivities (EDS) of all the complexes were tested, and the
8 results showed that their electrostatic sensitivities are remarkably higher than the human body
9 can generate, making them safe for laboratory handling (e.g., **1a**, EDS>44 J; **1b**, EDS>44 J;
10 static electricity from human body is 0.025 J). The sensitivities of these complexes are tunable
11 accompanying with the variation of modified groups on the ligand.
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23 CONCLUSIONS

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25 In summary, through changing different moieties such as NH₂, NO₂, NHNO₂ on the same
26 backbone bis-1,2,4-triazole, a series of energetic complexes were successfully designed and
27 synthesized. X-ray crystallography shows that as the modified groups of bis-1,2,4-triazole were
28 varied from NH₂ to NO₂, and then to NHNO₂, the densities of the resultant Cu-based complexes
29 enhance from 1.838 gcm⁻³ for **1a** to 1.978 gcm⁻³ for **2a**, and then to 2.049 gcm⁻³ for **3a**. Hence,
30 the detonation properties (detonation velocities and pressures) were tuned extremely well from
31 6454 ms⁻¹ and 18.61 GPa for **1a** to 6782 ms⁻¹ and 21.44GPa for **2a**, and then to 7103 ms⁻¹ and
32 23.98Gpa for **3a**. Moreover, energetic complexes based Zn ions also display a same trend.
33
34 Sensitivity tests showed that the impact sensitivities of **1a**, **1b**, **2a**, and **2b** are higher than 40 J,
35 while their friction sensitivities are higher than 360 N; thus, they are insensitive to impact and
36 friction. The electrostatic sensitivities of all the energetic complexes are extremely higher than
37 the those human body can generate, making them safe for laboratory handling. Therefore, this
38 work may provide an effective approach to modulate the energetic properties of complexes by
39 fine-tuning of energetic groups.
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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications web site at DOI: . The Supporting Information include details of X-ray crystallography such as additional figures, crystallographic data, and bond lengths and angles data for **1a-3a** and **1b-3b**, details of hydrogen-bonding interactions for **1a-3a** and **1b-3b**. and theoretical calculations for **1a-3b**.

Accession Codes

CCDC 1572530 (**1a**), 1572537 (**2a**), 1572502 (**3a**), 1030753 (**1b**), 1572538 (**2b**) and 1030755 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lishenghua@bit.edu.cn.

*E-mail: pangsp@bit.edu.cn.

Notes

The authors declare no competing financial interest.

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41 (54) According to UN recommendations on the transport of dangerous goods, impact:
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43 insensitive > 40 J, less sensitive \geq 35 J, sensitive \geq 4 J, very sensitive \leq 3 J. Friction: insensitive >
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45 360 N, less sensitive = 360 N, 80 N < sensitive < 360 N, very sensitive < 80 N, extremely
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47 sensitive < 10 N.
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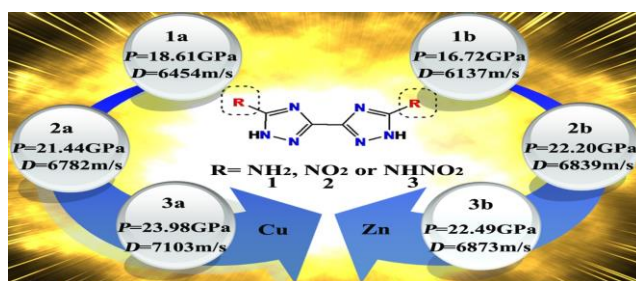
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3 (55) The room-temperature value was calculated by the volume expansion equation
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5 $\rho_{298K} = \rho_T / (1 + \alpha_v(298 - T)); \alpha_v = 1.5 \times 10^{-4} \text{ K}^{-1}$.
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Fine-Tuning the Energetic Properties of Complexes through Ligand Modification

Ji-Chuan Zhang, Hui Su, Shu Guo, Ya-Lu Dong, Shao-Wen Zhang, Tao Zou, Sheng-Hua Li, and Si-Ping Pang



A series of energetic complexes based on bis-1,2,4-triazole ligand were successfully designed and synthesized. The experimental results showed that as the modifying groups on the ligand were varied from NH₂, NO₂ to NHNO₂, the energetic properties of complexes were successfully tuned.