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D35. 含能材料（国际）

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D35-01

The Explosion Criterion for CHNO Assemblies and Alkali Metals

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We found that a combination of the hydrogen bond (X:H–Y or HB with ':' being electron lone pair of X = O or N, Y = X, C) tension and the super-HB (X:⇔:Y) or anti-HB (H↔H) compression, or the molecular proton/lone-pair number ratio, could form a criterion for judging whether an exploration happens. The X:⇔:Y and/or H↔H repulsion initiates but the X:H attraction constrains the explosion of substances such as LLM-105[1], TATB[2], and *cyclo*-N_5^-:[nH_3O^+; $(n\text{-}m)H_3O^+ + mNH_4^+$][3, 4] ($3 \le n \le 5$, $m \le n$) complexes. However, the absence of X:H–Y tension turns out spontaneous aquatic explosion of alkali metals Z or the molten alkali halides ZΩ, involving an intermediate process of ZHO solvation that produces the O:⇔:O super-HB by dissolving ZHO into Z^+ and HO^- with three pairs of lone pairs[5]. Conversely, the lack of X:⇔:Y repulsion fosters the explosion of neither the molten NaCl in liquid NH_3 nor the molten Na_2CO_3 salt or H_3BO_3 acid in water despite generating Na^+ and H^+. This bonding criterion may assist in efficiently devising explosives with the desired energy density and structural stability.

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D35-02

Synthesis of Advanced Pyrazole and N–N-Bridged Bistriazole-Based Secondary High-Energy Materials

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Recent attention in energetic materials research has been directed towards creating new compounds with improved energetic performance and decreased sensitivity to heat, shock, impact, and friction. Incorporating nitrogen-rich azoles into the framework has emerged as a promising strategy due to their ease of synthesis and ability to achieve the balanced performance. In this work, we have synthesised 3,5-dihydrazinyl-4-nitro-1*H*-pyrazole (**2**), 9-nitro-1*H*-pyrazolo[3,2-*c*:5,1-*c*']bis([1,2,4]triazole)-3,6-diamine (**3**), N-N bonded N,N'-([4,4'-bi(1,2,4-triazole)]-3,3'-diyl)dinitramide (**5**) and its stable nitrogen-rich energetic salts in a single or two-steps with quantitative yields from commercially available inexpensive starting material 4,6-dichloro-5-nitropyrimidine (**1**). Along with the NMR, IR, DSC, and elemental analysis (EA) characterization, the structures of almost all the compounds were confirmed by single crystal X-ray diffraction studies. Interestingly, most of the compounds show excellent thermal stability (ranges between 221 to 250 ℃) than RDX (210 ℃) and detonation velocities ranges from 8992 to 9069 m s^{-1} which are better than RDX (8878 m s^{-1}) and close to HMX (9221 m s^{-1}). All these compounds are insensitive to impact (10 to 35 J) and friction (360 N). The novelty, synthetic feasibility, and excellent energetic performance of all the molecules suggest that they can be used as potential secondary explosives in defence and civilian fields.

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D35-03

Azide Ionic Liquids for Safe, Green, and Highly-Efficient Azidation Reactions to Produce Azide Polymers

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Azide compounds are widely used and especially, polymers bearing pendant azide groups are highly desired in numerous fields. However, harsh reaction conditions are always mandatory to achieve full azidation, causing severe side reactions and degradation of the polymers. Herein, we report the design and preparation of two azide ionic liquids (AILs) with azide anion and triethylene glycol (E3)-containing cation, [P444E3][N3] and [MIME3][N3]. Compared with the traditional sodium azide (NaN3) approach, both AILs showed much higher reaction rates and functional-group tolerance. More importantly, they could act as both reagents and solvents for the quantitative azidation of various polymeric precursors under mild conditions. Theoretical simulations suggested that the outstanding performance of AILs originated from the existence of ion pairs during the reaction, and the E3 moieties played a crucial role. Lastly, after the reaction, the AILs could be easily regenerated, presenting a safer, greener, and highly efficient synthesis route for azide polymers.

D35-04

Performance Prediction of Energetic Materials Using Machine Learning Technology

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Currently, the development of energetic materials primarily relies on the experience and trial-and-error of researchers, which presents issues such as long development cycles, high costs, and significant safety risks. However, advancements in computer hardware and software, along with artificial intelligence technologies, have brought new opportunities to change the development model of energetic materials. In this context, by integrating machine learning and combinatorial chemistry techniques, we have developed a machine learning-assisted high-throughput virtual screening system for energetic molecules. This system can generate energetic molecules in high throughput and efficiently predict performance rapidly, covering comprehensive properties (including density, detonation velocity, detonation pressure, heat of formation, decomposition temperature, melting point, and impact sensitivity). Further research based on this system has shown that the prediction of energetic properties (such as density, detonation velocity, detonation pressure, and heat of formation) tends to be more accurate, with coefficients of determination typically exceeding 0.75, while the accuracy for stability-related parameters (such as thermal properties and impact sensitivity) is relatively lower, usually around 0.6. To explore the possibility of improving the prediction accuracy of thermal behavior-related performances, we applied graph neural networks to predict the melting points of energetic materials. The study demonstrated that graph neural networks have superior molecular representation capabilities compared to general molecular descriptors and molecular fingerprint, which can enhance the accuracy of melting point predictions. Moreover, introducing descriptors based on prior knowledge for energetic molecules remains a potent approach to improve prediction accuracy. Lastly, for the prediction of thermal decomposition temperature, we experimented with a variety of feature extraction methods and combinations of machine learning algorithms, achieving improved prediction accuracy. Using the SHAP method, we analyzed the output of the decomposition temperature model, identifying crucial molecular descriptors that significantly impact decomposition temperature, with the aim of providing references for subsequent model optimization and improvement.Our research work demonstrates that using machine learning to predict the performance of energetic molecules is feasible. However, improving the predictive accuracy for stability-related properties still requires further study. It is necessary to approach this from multiple aspects, including deeper research into the structure-stability relationship of energetic materials, data quality, feature representation, and model algorithms, in order to potentially achieve a high generalization capability and high accuracy in the predictive model for energetic materials.

D35-05

Covalently linked Carborane Clusters with ZIF for High-Efficiency Hypergolicity

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Crystalline framework has long been a research frontier in material science. Recently, energetic crystalline framework received considerable attention as illuminate by the potential benefits of the development of interdisciplinary. However, the well-developed porosity of crystalline framework greatly reduced the energy density of energetic material, resulting in lower output energy. A custom-modified approach to improve the energetic performance are urgently required. Thiol-yne click reaction possess the advantages of fast reaction rate, and facile reaction conditions, yet rarely used in modification crystalline framework. As a proof of concept we introduce energy-rich, size-matched and reductive 1,2-dicarbadodecaborane-1-thiol (CB-SH) into a acetenyl groups fictionized hypergolic MOF Zn(AIm)2, Zn(AIm)2-CB via hiol-yne click reaction, resulting in an energy density increase as high as 46.6% and up to 44.6 % improvement in combustion enthalpy. Moreover, the ignition rate greatly accelerates due to the reducibility of carboranes, and the ignition delay time (4 ms) is shorted by sixfold with red fuming nitric acid as the oxidizer. The incorporation of carboranes into the MOF skeleton also stabilizes the resulting materials toward external mechanic stimuli. The mechanism by which the CB-SH promote hypergolic ignition was studied via density functional theory calculations. The thiol-yne click modification strategy presented here is simple and powerful, and permits engineering of crystalline framework materials for the design of advanced energetic materials.

D35-06

Low sensitive high energetic materials achieved through assemblying

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The assembly of strategy was used to design and synthesize new energetic materials, which were composed by energetic acid and base, more than 10 new energetic compounds with excellent detonation properties, low sensitivity, and high stability were prepared in aqueous simply. Most of them were characterized by IR, NMR, sensitive test, TG-DSC, X-ray single structure. With heat of formation, density and formula in hand, all of their detonation properties were calculated by EXPLO 6.07 version. Several of them with superior detonation velocity and higher decomposition temperature than those of RDX. Given that their simple synthesis, excellent energetic properties and low sensitivities, at least 5 new energetic compounds show promising.

D35-07

Construction Strategy of Dense Spherulite of HNS via Specific Adsorption of Antisolvent Combined with Polymer

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The application value of micro-nano hierarchical structure has been widely recognized in many fields, as it can greatly improve the surface performance of particles. Furthermore, the advantages of micro-nano hierarchical structure also bring new opportunities for the performance regulation of energetic materials, as an important material for both civilian and military applications, whose performance directly affects the application areas. This work developed a novel strategy for controlling the construction of dense spherulite of 2,2’,4,4’,6,6’-hexanitrostilbene(HNS) by utilizing antisolvent specific adsorption to generate noncrystallographic branching combined with the polymer additive to inhibit diffusion. Computational simulations revealed that toluene (TOL) exhibits specific adsorption on the (100) face of HNS through π-π interactions, while the polymer additive (Poly(acrylic acid), PAA) strongly interacts with each crystal face of HNS through hydrogen bonding, effectively inhibiting diffusion. Based on these findings, dense spherulites of HNS were successfully prepared by controlling supersaturation. The HNS spherulites exhibited superior fluidity, specific surface area, porosity, and impact sensitivity. This work not only validates the effectiveness of antisolvent-induced branching in constructing dense spherulite structures, but also provides valuable insights into controlling crystal morphology. Furthermore, this research offers a promising approach to enhancing the safety and performance of energetic materials.

D35-08

Multi-ionic integrated energetic materials

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In response to the long-term challenges of high explosive performance, high stability, and low cost in the development of practicable energetic materials, we have proposed and developed a family of multi-ionic integrated energetic materials that could be prepared via a simple one-pot reaction under ambient condition by using low-cost raw chemicals. Each reductive organic cation is encapsulated in a cage-like unit of inorganic anionic framework. Such an alternate and dense packing of oxidative anions and reductive organic cations endows these materials with a high structure stability by the attractive electrostatic Coulomb forces, meanwhile endows them with a good detonation performance via very rapid and high efficient redox reactions in decomposition. For instant, a metal-free compound called DAP-4, which could be synthesized from assembly reactions between 1,4-diazabicyclo[2.2.2]octane and ammonium perchlorate in a yield of higher than 90% under ambient conditions in an aqueous solution, has a high detonation performance comparable with RDX and HMX, and a much higher thermal stability and lower cost. We have achieved controllable preparation of DAP-4 in large scale, developed DAP-4 based heat-resistant explosives for loading perforating charges, and achieved excellent application results in the application of high power heat-resistant explosives. As a new kind of low-cost non-nitro energetic materials, the multi-ionic integrated energetic materials open a new avenue for designing advanced energetic materials for practical uses.

D35-09

Iron as a recyclable metal fuel for storage and transportation of energy and substitution of coal in power plants

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Climate crisis effects are raising commitments towards decreasing green-house gas emissions from energy sector. Renewable electricity is typically seasonal and cannot provide a stable, predictable and on-demand source of energy. Storing electrical energy for long periods and transporting it over long distances is an essential task of the necessary transition to a CO2-free energy economy. Metal fuels are potential candidates for chemical energy storage/release through oxidation–reduction cycles. Iron and its oxides represent a very promising technology in this regard, due to its ideal balance of properties such as energy density, cost and availability. Moreover, these properties allows iron to be a substitute for coal in power plants, allowing the retrofitting of a vast number of soon-to-be decommissioned power stations. In this work we investigate the feasibility of using this resource as an energy carrier through the availability of the essential materials and infrastructure in the supply chain. Then, we investigate the technical requirements and modifications for retrofitting one power plant, estimating the costs of the retrofitting process and the achievable energy conversion efficiency. Finally, we look into the logistic operations for production, storage and transportation of this fuel, estimating the levelized cost of electricity and round-trip energy efficiencies for the whole cycle, comparing to traditional fossil fuels and H2. This study has demonstrated that iron is a promising energy carrier for the energy transition, putting into evidence the most significant bottlenecks that must be overcome to achieve a sustainable production and utilization of this material.

D35-10

Defect engineering in ultrafine explosives: Characterization, regulation, and performance

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Ultrafine explosives show high safety and reliable initiation, and have been widely used in aerospace, military, and industrial systems. The outstanding performance of ultrafine explosives is highly related to the high specific surface area of ultrafine particles. Recent simulation results indicated another factor, i.e. the nano-void defect, that largely affect the performance of ultrafine explosives. However, rare experimental results of the nano-voids in ultrafine explosive particles have been reported. In this work, internal nano-voids in ultrafine explosives 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) and 2,2′,4,4′,6,6′-hexanitro diphenylethylene (HNS) have been reliably measured by contrast-variation small angle X-ray scattering. Liquid nitrogen quenching during heating process was applicated to regulate the internal nano-voids in ultrafine LLM-105, which could inhibit solid phase ripening that decreases the specific surface area. The thermal stability of ultrafine LLM-105 was remarkably improved via changing the structures of nano-voids. This work may pave the path to enhance the performance of ultrafine explosives via defect engineering.

D35-11

Simulation of the mechanical properties of HTPB-based composite propellants

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This study investigates the mechanical properties of a hydroxy-terminated polybutadiene (HTPB)-based composite propellant using molecular dynamics (MD) simulations. The propellant model incorporates core-shell structures representing aluminum and oxidizer particles embedded within the HTPB matrix. Young's modulus, tensile strength, and maximum elongation were evaluated using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package. A validated force field developed by a research group at the Beijing Institute of Technology was employed to describe the interatomic interactions within the propellant system. The obtained MD simulation results were compared with experimental data from uniaxial tensile testing conducted on propellant samples at various temperatures and strain rates. The simulations yielded mechanical properties that were in good agreement with the experimental measurements. However, slight deviations were observed, potentially attributable to limitations in the simulated system size and the accuracy of the applied force field for the specific propellant composition. This work demonstrates the potential of MD simulations as a tool for evaluating the mechanical response of HTPB-based composite propellants, paving the way for further investigations into the influence of propellant composition and microstructure on mechanical behavior."

D35-12

Design and synthesis of "full nitration+" energetic materials

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Generally speaking, the higher the number of nitro groups, the higher the energy of the energetic materials, but the stability will be significantly reduced. For example, the hexanitrobenzene HNB, which realizes the full nitro substitution on the benzene ring, has a high energy, but the explosive decomposition occurs in humid air, which seriously restricts the application of the full nitration materials. In order to further improve the energy and stability of traditional fully nitrated materials, the present work proposes the “full nitration +” construction strategy, which combines the fully nitrated structure with high-energy bond, strong H-bonding, strong conjugation, and homogeneous charge, and improves the stability on the basis of retaining/even further increasing the energy of traditional fully nitrated materials, so that a series of novel “full nitration +” materials are designed and synthesized. Meanwhile the structure-performance relationship of these materials was investigated and to provide new insights into the development of high-energy and high-safety energetic materials.

D35-13

Advanced Energetic Materials Based on 4-Substituted-3,5-Dinitropyrazoles

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High Energy Density Materials (HEDMs) have significantly benefitted the progress of humankind, increasing its demand for both military and civilian applications. Explosives have been used to mitigate various difficult undertakings, including mining, construction projects, metal cutting, oil drilling, space explorations, etc. Contemporary research in the field of energetic materials has been essentially focusing on the synthesis of environmentally friendly, stable and insensitive explosives, apart from their high-performing characteristics.

New-age energetic materials have been primarily comprised of nitrogen-rich heterocyclic rings like pyrazole, tetrazole, oxadiazole, etc., due to the desired energetic performance arising from many N-N and N-C energetic bonds. 3,5-Dinitropyrazole-based compounds, for instance, have been extensively explored owing to their high nitrogen and oxygen content, high heats of formation, and adequate densities. 4-substituted-3,5-dinitropyrazole-based energetic compounds are the most explored, and their properties can be controlled depending on the substituent on the 4th position. Substituents capable of intramolecular hydrogen bonding (e.g., -NH2 and -OH) tend to improve the stability of resulting compounds, whereas electron withdrawing substituents (e.g., -NHNO2, -NO2) make them sensitive. 4-Azido-3,5-dinitropyrazole (AzDNP) with 49.35 % nitrogen content and high positive heat of formation ($\Delta Hf = 473$ kJ/mol) is a good contender for green energetic materials.

In this work, we have synthesized varoious green energetic materials consisting of 4-hydroxy-3,5-dinitropyrazole, 4-azido-3,5-dinitropyrazole and 4-carboxy-3,5-dinitropyrazole moieties. This presentation will present the synthesis, characterization, and energetic properties determination of advanced nitrogen-rich mixed azoles-based green energetic materials. Different approaches are used for fine-tuning the properties by connecting various types of energetic moieties using alkyl bridges, metal-catalyzed cross-coupling reactions, and energetic salt formations. Many of the synthesized compounds have energetic properties better than RDX (1,3,5-Trinitro-1,3,5-triazinane). These compounds will be highly useful for various military and civilian applications.

D35-14

Probing the Detailed Chemical Kinetic Mechanism of Hydrazine Propellants Combustion

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Unsymmetrical dimethylhydrazine (UDMH) and methylhydrazine (MMH) are both derivatives of hydrazine (N2H4), with each having additional methyl groups (-CH3) attached to the nitrogen atoms in different arrangements. These substances are used as rocket propellants due to their energetic properties but also pose significant risks due to their toxicity and volatility. UDMH and MMH is a liquid at room temperature and is commonly used in combination with nitrogen tetroxide (N2O4) as a hypergolic propellant in bipropellant systems.

This talk focuses on the detailed chemical kinetic mechanism development of UDMH and MMH combustion, the work includes the quantum chemical calculation of the key elementary reactions and species, the fundamental ignition and combustion experiments, and the detailed kinetic model development and validation.

D35-15

Preparation of Novel High-performing Energetic Bi-component Compounds by Proton-transfer from Pyrazole to Tetrazole

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Precise tuning on the acidity of *N*–H is crucial to the forming of high-performance energetic bi-component compounds. In this work, two strategies were applied to enhance the weak acidity of the pyrazole *N*–H in 4-nitro-3-(1*H*-tetrazol-1-yl)-1*H*-pyrazol-5-amine (**1**), *i.e.*, introduction of nitro group via nitration and proton-transfer from pyrazole to tetrazole. Initially **1** could only form a cocrystal with hydrazine due to its low acidity. With the introduction of nitro group, the pyrazole *N*–H was still not able to deprotonate. However, with a proton-transfer from pyrazole to tetrazole, the acidity of **1** was strengthened which allows **1** to react with bases to form energetic salts. All the newly prepared compounds exhibit excellent detonation performances (D = 8153–9292 $\mathrm{m{\cdot}s^{-1}}$, P = 24.3–33.4 GPa). Moreover, all the energetic compounds produce high gas volumes (794.6–820.1 $\mathrm{dm^3\ kg^{-1}}$), and are expected to be utilized as gas generators.

D35-16

Structural evolvement of typical melt-cast explosives under high pressure

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Modern warfare has very high requirements for the damage effect and survival ability of weapons under complex environments. Explosives are the energy source of weapons' power and damage system. So the detonation performance, effectiveness and safety of explosives are extremely important. High pressure can influence the state, crystal and micro structures, therefore, greatly affect decomposition, energy release characteristics, safety and stability of explosives. The melt-cast explosives exhibit the advantages of low cost and simple synthesis process, and have been widely used. The mixed explosives based on melt-cast explosives account for more than 90% of the military mixed explosives. Understanding the structural variations of melt-cast explosives helps to construct the state evolvement model, give insight into the decomposition, initiation performance, detonation properties and safety.

This study explored the structural evolvement of typical melt-cast explosives, α-DNAN and MTNP. For the weak intensity of intermolecular interactions, α-DNAN can be compressed easily and a pressure-induced phase transition may happen. In situ high-pressure Raman spectra suggested that α-DNAN did exhibit a phase transition at 1.5 GPa and had the tendency to be amorphous at higher pressures. The high-temperature and high-pressure Raman and photographs investigation of α-DNAN illustrated that pressure will significantly influence the melt temperature. The melt point increased at pressures. When the pressure reached 1.9 GPa, the decomposition happened accompanied with melting process. MTNP underwent a phase transition at 8.7 GPa. In addition, a irreversible pressure-induced amorphization occurred above 15.3 GPa. This study achieved the high-pressure stability and structural evolvement of two explosives, built the relationship between weak intermolecular interactions and high-pressure structural stability, helped to construct the high-pressure reaction equation of state, and provided the scientific basis to understand their detonation process.

D35-17

Facile Synthesis of advanced high-energy density material with fine-tuned property

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The continuous drive of researchers around the world pushes them to develop energetic material with a fine balance between energy and stability. The quest for new energetic materials is mainly challenging because these materials need to satisfy the stringent requirements of a good oxygen balance, high density, positive energy content, high detonation properties, high thermal stability, less sensitivity, low environmental toxicity, easy synthesis, etc. Achieving this contradictory requisite is complicated as performance and stability are associated closely with the molecular structure. Among the vast class of Nitrogen-rich heterocyclic backbones, fused moieties, and oxadiazoles are noteworthy due to their practicality, and diversity in their energetic properties. The 1,3,4-oxadiazole, despite being less explored, offers a symmetric, planar ring with reduced steric hindrance due to two non-vicinal positions available for substitution, making it suitable for energetic materials. In this regard, we have synthesized 5,5′-dinitramino-3,3′-azo-1,3,4-oxadiazole and its energetic salts. Additionally, fused backbones with extended conjugation and ring strain energy results in more stable yet powerful molecules. Pyrimidine and triazine are exceptional compounds due to their high energy content and demonstrated prospective applications in energetic materials. Pyrazole-fused 4-amino-1,2,3-triazine N-oxides and 4-amino-pyrimidine 5-oxide, as well as pyrazole-fused pyrimidine nitramide and its N-oxide derivative, have been synthesized in this regard. The 1,3,4-oxadiazole-based compounds with acceptable insensitivity exhibit high density (1.82-1.97 g/cm^3) and excellent detonation parameters (VOD: 8333-9358 m/s, DP: 25.5-39.1 GPa). Moreover, fused pyrazole moieties are highly insensitive (IS: >35J, FS: >360 N) with good density (1.65-1.85 g/cm^3). Especially, pyrazole and pyrimidine-substituted compound along with outstanding thermostability (Td: 338°C), also demonstrate fluorescence property which can be used as energetic fillers for easy detection. Together, the advantages of reaction efficiency, availability of commercial reagents, and attractive energetic properties indicate the scope of synthesized compounds as secondary energetic materials in civil and military applications.

D35-18

Structural and Morphological Regulation of Micro-Nano Energetic Materials Based on Microfluidic Methods

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The study on the structural and morphological regulation of micro-nano energetic materials was approached from three key perspectives: crystal form manipulation, micro-nano hierarchical structure, and core-shell composite structure. Utilizing microfluidic techniques, distinct crystallization systems were engineered and models were developed for structural and morphological regulation through molecular dynamics simulations. This resulted in the successful preparation of different CL-20 crystal forms, HNS microspheres with spherical hierarchical structures, and HMX@FOX-7 core-shell composites. The core part of microfluidic system was the coaxial micromixer, which enabled us to efficiently convert α-CL-20 to β-CL-20 by finely tuning the flow rate ratio of anti-solvent to solvent under microscale conditions. In gas-liquid Taylor flow, α-CL-20 to ε-CL-20-PBX were prepared by altering the concentration of the CL-20 solution. Employing an oscillating-swirling-coflowing microfluidic crystallization system, the suspension characteristics were controlled by adjusting the flow rate ratio, achieving the regulation of HNS micro-nano hierarchical structures' integrity and sphericity. The HNS microspheres exhibited an impact initiation threshold on par with nano-HNS, with an ignition voltage of 1400 V. Similarly, by considering the influence of crystallization sequence, and binding strength on the explosive composite structure, the best core-shell structure and sphericity of HMX@FOX-7 can be achieved when the composite ratio is 1:1 in the co-coating mode of two components. The HMX@FOX-7 composite explosive microspheres demonstrated a 52% reduction in impact sensitivity, a 75% decrease in friction sensitivity, a 36% increase in burning rate, and a superior effect on enhancing the burning rate in composite propellants compared to homogeneous mixtures. By integrating these three aspects of structural and morphological regulation, microfluidic methods have demonstrated the ability to assemble fine crystal structures and the regulate particle morphology of energetics materials under microscale flow conditions, offering innovative approaches for the precision and controllable safe manufacturing of micro-nano energetic materials.

D35-19

Interpretable and Physicochemical-Intuitive Deep Learning Approach for the Design of Thermal-Resistance of Energetic Compounds

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Thermal-resistance of energetic materials are vital because of their direct impact on the safety and sustainability. However, developing precise and interpretable prediction models for thermal resistance is challenging due to limited data availability and a lack of quantitative structure-property insights. Leveraging the capability of deep learning to revolutionize material discovery, a robust deep learning framework called EM-thermo is proposed. To tackle the obstacle for data availability, a dataset encompassing 5029 CHNO compounds and their thermal-resistance is constructed, with 976 belonging to energetic compounds. EM-thermo utilizes molecular graphs and direct message-passing neural networks, and demonstrates a versatile framework to represent structural features of compounds and to correlate them with properties. Through transfer learning techniques, EM-thermo enables the prediction of thermal-resistance of energetic compounds (decomposition temperature above 573.15 K). EM-thermo is utilized to forecast thermal-resistance with an accuracy around 99% and thermal decomposition temperatures with a mean absolute error around 30 K. Model performances underscore the significance of rational deep-learning framework than molecular feature selection in enhancing predictive accuracy. Consequently, we assert that EM-thermo enables chemists to uncover dependable structure-property relationships for energetic compounds, providing valuable insights to inform molecular discovery.

D35-20

Synthesis of Energetic Materials through Skeleton Editing

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Single-atom skeletal editing has recently emerged as a powerful synthetic strategy, allowing precise and direct modification to the core skeleton of organic molecules. Thus, one could rapidly evaluate the potential interest of energetic analogues by interchanging the nature of one (or more) aromatic ring(s). This paradigm shift would greatly accelerate energetic materials development and prevent time consuming and in-depth retrosynthetic analysis to access complex analogues through nontraditional disconnections. In this report, we developed a unified and standardized sequence to synthesize three types of bipyrazole skeletons through skeleton editing strategies. This mode enables rapid bipyrazole syntheses with simple reagents and is favorable for practical synthetic applications. And based on this, a series of energetic molecules were synthesized.

D35-21

Computational Methods and Software Development for Accelerating Energetic Materials Design

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The molecular crystal structure of energetic materials serves as the foundation for exploring their other crucial properties. Predicting these structures, particularly for energetic materials, involves two major challenges: (1) accurately and rapidly calculating the energy of given crystal structures and (2) efficiently locating the global energy minimum or metastable structures on the potential energy surface. To address these challenges, we have developed the nonlocal subsystem density functional theory (NL-sDFT) for first-principles electronic structure calculations. This method employs a divide-and-conquer approach, significantly improving both the accuracy and speed of calculations for weakly interacting systems composed of numerous molecules, such as molecular crystals, compared to conventional DFT methods. In terms of structure search, we have extended the CALYPSO structure prediction method, significantly enhancing prediction efficiency. Leveraging these methods, we have successfully predicted more than 20 reported pentazole ionic salts and other nitrogen-rich ion salts. These developed methods and software provide effective tools for the design of energetic materials.

D35-22

Exploring the potential use of biogas as a feedstock for producing high surface area zeolite templated carbons for hydrogen storage applications

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Biogas, a product of anaerobic digestion, is an attractive renewable energy source due to its continuous production and use cycle. Recently, there has been great interest in the value addition of biogas concerning the utilisation of the main component (i.e methane, CH_4). In our recent study, we focussed on the thermocatalytic decomposition (TCD) of methane, using substituted LaNi1-xCuxO_3 perovskite catalysts as an attractive alternative to produce low-carbon hydrogen and solid carbonaceous materials. In this study, we explored the potential for utilisation of simulated biogas (CH_4 and CO_2 mixture) and pure CH4 for the synthesis of zeolite-templated carbons (ZTCs). ZTCs have attractive properties such as large surface area, uniform pores and high pore volumes, and have found applications in a wide range of attractive applications such as gas storage, CO_2 capture, supercapacitors and batteries. When methane was utilised on both the one-step and two-step processes, the obtained ZTCs had higher surface area and hydrogen (H_2) adsorption. Structural (XRD) and morphological (SEM and TEM) characterisation were found to be almost similar to the samples obtained when fossil-derived ethylene was used as a carbon source. This study has demonstrated that a sustainable source of carbonaceous feedstock (biogas-derived ‘biomethane’) can be utilised to produce value-added products (ZTCs), which can open additional economic benefits for companies or industries engaged in the biogas sector.

D35-23

Predicting the Burning Rate of NEPE Propellants Based on the Detailed Combustion Kinetic Mechanism

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Solid propellants are vital energy sources for the performance of missiles and rocket engines, necessitating their development with a focus on energy density and combustion sensitivity. Nitrate Ester Plasticized Polyether (NEPE) propellant, a novel, high-energy solid propellant, consists of mixed nitrate ester plasticized polyether as the adhesive, solid oxidants like Ammonium perchlorate (AP), aluminum as metal fuel, and high-energy explosives such as octogen (HMX). This composition results in a high-pressure index and a narrow range of adjustable burning rates. However, there are challenges in adjusting combustion performance due to constraints between burning rate and pressure index adjustment technology. Additionally, existing solid propellant combustion mechanisms are ineffective for simulating the combustion process of NEPE propellants. This study develops a detailed chemical kinetic model for accurately predicting the burning rate of NEPE propellant. Specifically, a comprehensive gas-phase and liquid-phase reaction kinetics mechanism is developed by integrating detailed gas-phase combustion kinetics, solid-phase pyrolysis reaction mechanisms of NEPE propellant, solid-phase pyrolysis reaction rates, burning surface displacement models for NEPE formulations with polyethylene glycol (PEG), nitroglycerin (NG), 1,2,4-butanetriol trinitrate (BTTN), HMX, AP, and Al. The gas-phase reaction kinetic mechanism analyzes the sensitivity and reaction flux of the NEPE propellant combustion process, identifying key pyrolysis and combustion products, free radicals, and key elemental reactions across a wide range of equivalence ratio and pressure conditions. The modified prediction model accurately predicts the combustion rate of the vital oxidant HMX in NEPE and its formulation over a wide pressure range. Theoretical calculations are conducted on the propellant's gas-phase and solid-phase burning surface temperatures, and the model simulates with good agreement with relevant propellant burning rate testing experimental data from the literature. These research findings are significant for advancing the development of composite propellants, particularly high-energy propellants, and enhancing the performance level of rockets and missiles.

D35-24

Engineering agglomeration and reaction propagation of nano energetic composites

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Energetic nanocomposites such as nanothermites are attracting increasing attention for their high enthalpy of reaction, making them potential additives in propellants and explosives to increase the overall energy density. This unique category, which has both military and civilian applications, is limited in widespread implementation due to the inherent complexity of heterogeneous combustion that has yet to be fully understood. One of the major concerns is the loss of nanostructure during reaction —named agglomerating or reactive

sintering — plays a significant role in the combustion performance of nanothermites by rapidly melting and coalescing aggregated metal nanoparticles, which increases the initial size of the reacting composite powders before burning. Here, we demonstrate a high-speed microscopy/thermometry capability that enables ~ μs time and ~ μm spatial resolution as applied to highly exothermic reaction propagation to directly observe the agglomerating and the reaction front at high spatial and temporal resolution. The reaction front thickness, thermal gradient, and local microscopic and macroscopic propagation rate were investigated and the relationship between agglomerations and propagation was probed based on the heat transfer mechanisms. Based on the new learnings, various approaches of engineering the agglomeration and reaction propagation approaches were demonstrated.

D35-25

Heterometallic energetic complexes as a smart platform for combustion catalysts of solid propellants

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Owing to their significant application potential in combustion catalysts of solid propellants, the development of energetic complexes (ECs) with high energy and catalytic ability has attracted great attention in recent years. The structures and performance of ECs can be effectively regulated through the reasonable combination of energetic ligands and metal centers. Herein, a heterometallic strategy was explored for preparing novel ECs as combustion catalysts for high energy solid propellants. Through this strategy, three novel ECs (1-3) were formed with Cu2+ ion as the main metal centers and alkali metal ions, i.e., Na+, K+, and Rb+ as the second metal centers. The structures and performance of those ECs were comprehensively studied. Single crystal X-ray diffraction showed that compound 1 had a layered structure, while compounds 2 and 3 had three dimensional skeletons. All the materials had great densities, the highest density value was observed in compound 3 as 2.404 g·cm-3. Moreover, those materials had excellent thermal stability. The decomposition temperatures were higher than 247 oC. The highest value was observed in compound 1 as 300.8 oC. All materials had great mechanical sensitivity. The impact sensitivities and fraction sensitivities were better than 20 J and 240 N, respectively. In addition, the catalytic combustion performance of these materials on high energy solid propellant was also investigated. Within the pressure range of 3-10 MPa, using these complexes as combustion catalysts significantly improved the combustion performance of the examined solid propellant. The combustion ratio can be increased by 42%, and the pressure index can be reduced to 0.43. The great comprehensive performance and excellent catalytic ability of these materials make them have great application potential as combustion catalysts for high energy solid propellants.

D35-26

Performance Regulation and Damage Application of Multicomponent Aluminum-Based Energetic Composites

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Energetic composites are a class of materials composed of reductants and oxidants that can independently undergo chemical reactions upon activation, releasing a large amount of heat in a short period and producing high-temperature molten products. Pyrotechnic cutting technology utilizes the high-temperature molten products generated by the combustion of energetic composites within a cutting torch. These products form a molten jet with high thermal energy, high kinetic energy, and high fluidity through the nozzle, which melts and impacts metal targets, thereby achieving the purpose of cutting the target metal. For metal cutting applications, energetic composites need

to have high reaction enthalpy, an appropriate combustion rate, and gas production performance. Based on aluminum-based energetic composites, a strategy of regulating energy release characteristics through multicomponent composition was adopted. Multi-component energetic agents were prepared using the compression molding process. The combustion performance of the powders and bulk materials was systematically characterized using a combustion performance characterization platform. Key performance such as self-propagating combustion characteristics, constant volume reaction pressure, and ignition or reaction delay time were evaluated. The influence of the component system on the combustion performance of multicomponent energetic composites was elucidated. A cutting torch prototype was developed to verify the cutting performance of the multicomponent energetic agents on steel plates, specifically targeting the application of energetic agents for oil pipe cutting.

D35-27

Design and Construction of Novel Laser-Sensitive Primary Explosives

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Pyrotechnics are the devices and systems that complete ignition, detonation, and work in weapon systems. Their safety, reliability, and effectiveness are directly related to the effectiveness of weapon systems, launch vehicles, and space vehicles. Laser-sensitive initiation is a new type of initiation technology which is safe, reliable and light. Firstly, there are no bridge wires, flyers and leads in the system, which avoids accidental ignition caused by electromagnetic pulse and other interference signals, and also avoids resistance change or fracture caused by bridge wire corrosion, ensuring the reliability of initiation; Secondly, the system no longer uses the primary explosive that is sensitive to conventional stimuli such as impact and thermoelectricity, making it safer in production, transportation and service processing; Thirdly, the system does not need energy exchange components, which can make the detonating device more portable and miniaturized, and the utilization rate of laser energy is higher. Finally, the system also has the characteristics of high accuracy, good instantaneity, simple and safe, and low cost. Therefore, laser direct detonation technology is in line with the development trend of insensitive ammunition, and is an important direction of the development of advanced detonation technology.

At present, the development obstacle of laser direct detonation technology is mainly restricted by the laser-sensitive primary explosives. To this end, our team innovatively integrated the forms of coordination polymers, chelates, cocrystals and other crystal materials with laser-sensitive primary explosives, and theoretically broke through the problems of high detonation threshold caused by poor safety, low energy output and poor photosensitivity of current laser-sensitive primary explosivess. A series of new laser-sensitive primary explosives with low sensitivity, high energy and high efficiency laser response were designed and constructed, which laid the foundation for the rapid development and application of laser direct detonation technology and opened up new ideas for the development of new laser detonators.

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D35-P01

Designing new heat-resistant energetic materials through a combined strategy of extended π-conjugation and hydrogen bonding network

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With the increasing demand for deep oil well resources and rapid development of aerospace exploration, the search for advanced heat-resistant energetic compounds has attracted the attention of researchers in the field of energetic materials.[1-3] In this study, two heat-resistant energetic materials, viz. 3,6-bis(3,5-diamino-4-nitropyrazol-1-yl)-1,2,4,5-triazine (**NPX-01**) and 2,4,6-tri(3,5-diamino-4-nitropyrazol-1-yl)-1,3,5-triazine (**NPX-02**) were designed and synthesized through designing a strong hydrogen bonding and extended π-conjugation synergistic strategy.[4] The thermal decomposition temperatures of **NPX-01** and **NPX-02** reached 370.4 °C and 387.7 °C, respectively, which are even higher than those of commonly used heat-resistant energetic materials such as TATB (T_d=360.0 °C) and PYX (T_d=360.0 °C). Moreover, **NPX-01** and **NPX-02** also exhibited good detonation velocity (D=8769 m s^{-1} and D=8310 m s^{-1}, respectively) and low mechanical sensitivities (IS≥40 J, FS>360 N), demonstrating their great potential as novel heat-resistant energetic materials. The influence of amino-nitro alignment and π-conjugation on thermal stability of these compounds was further studied by theoretical modeling calculations. The findings of our study highlight the significant advancements made in achieving ultra-high heat resistance in energetic materials through innovative design strategies.

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D35-P02

Intramolecular Integration of Bis (4-Nitropyrazole-1,2,4-triazole) Heterocyclic Skeletons: A New Tetracyclic Heat-resistant Energetic Framework

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Currently, within the realm of high-energy material research, the foremost priority lies in the pursuit of harmonizing exceptional performance and molecular stability. In this study, the high energy portion of bis (4-nitropyrazole) was successfully combined with the highly stable portion of 1,2,4-triazole through intramolecular integration strategy, resulting in the construction of an advanced tetracyclic framework. Two tetracyclic heat-resistant explosives 3,3'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(1H-1,2,4-triazol-5-amine) (3) and 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis (4H-1,2,4-triazole-3,4-diamine) (4) with excellent comprehensive performance have been successfully prepared. In particular, compounds 3 and 4 exhibit outstanding detonation performance (3: Dv = 8402 m/s, P = 27.79 GPa; 4: Dv = 8675 m/s, P = 29.62 GPa) and good thermal stability (3: Td = 354 °C; 4: Td = 346 °C). Notably, compound 4 showcased a notable detonation velocity of 8675 m/s, surpassing the conventional heat-resistant explosive HNS with a velocity of 7164 m/s. Furthermore, compared with HNS (Td = 318 °C; IS > 40 J; FS > 360 N), compound 4 not only has higher thermal stability (Td = 346 °C), but also exhibits lower sensitivity (IS > 40 J; FS > 360 N). These special properties give it the potential to become a novel type of heat-resistant and insensitive energetic material.

D35-P03

The introduction of trinitromethyl into 1,2,4-oxadiazol to reduce sensitivity

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Herein, a new series compounds based on 1,2,4-oxadiazol-5(4H)-one was synthesized. The molecular structure and thermal stability were confirmed utilizing various techniques, including NMR (^{1}H and ^{13}C) spectroscopy, X-ray diffraction analysis, IR spectroscopy, and differential scanning calorimetry (DSC). The results uncovered that compound **3** with trinitromethyl exhibited a higher decomposition temperature (T_d = 143 °C) compared to 3-(dinitromethyl)-1,2,4-oxadiazol-5-one (**A**) (T_d = 76 °C) recorded in the literature. Furthermore, according to the sensitivity test, compound **3** presented the lower friction and impact sensitivities (IS = 10 J, FS = 120 N) than **A** and **RDX** (IS = 6 and 7.4 J, FS = 40 and 120 N). In order to further investigate the difference between compound **3** and **A**, charge distribution and Hirshfeld surface were calculated to study their intermolecular interactions. The varying stability of these compounds was observed to primarily stem from intermolecular hydrogen bonds. Overall, the statistical data demonstrated the application potential of compound **3** as an energetic material.

D35-P04

Study of work-heat conversion properties under frictional behavior conditions at the interface of high-energy β-HMX crystals

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Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazacycloheptane (β-HMX) is widely used in high explosives due to its excellent mechanical properties and low sensitivity, however, frictional behavior is unavoidable during its manufacture, transportation and use. It is crucial to understand the effect of friction on the temperature rise at the interface of β-HMX, as the frictional heating at the crystal interface can induce its ignition and explosion. In this study, the friction behavior and surface temperature of beta-phase octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β-HMX), a widely used energetic crystal in the modern weapon industry, is systematically investigated by varying the contact pressure and sliding speed as well as sliding cycles. Experimental results reveal that the maximum temperature rise on the β-HMX surface can be well correlated with the frictional power density involving the friction coefficient and nominal contact pressure and sliding speed. The frictional work-heat conversion rate of β-HMX surface decreases with the frictional power density and then stabilizes at ~43.7% upon a single scratch and it decreases with sliding cycles upon reciprocating scratch. These findings can provide deep insights into the frictional safety of energetic materials.

D35-P05

Crystal Structure Predictions and Properties Explorations of Nitrogen-rich Energetic Materials

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Nitrogen-rich materials are promising environmentally friendly high energy density materials. The crystal structure predictions (CSP) are crucial to explore unknown energetic materials due to their low cost, safety and effectiveness. However, the traditional CSP method, guided by "lowest energy", suffer great challenge due to the intrinsic metastable properties of energetic materials.

Recent years, we proposed an effective CSP method to overcome the above challenge via assembling coordinated cations and nitrogen-rich anions. Using this method, we proposed a series novel stable nitrogen-rich energetic materials such as $Be(N_5)_2$, $Mg(N_5)_2$, $Al(N_5)_3$, $C(N_5)_4$ under ambient conditions. The research results indicate that high-valence cations not only can provide electrons to stable to pentazolates but also increase the energy density and detonation performance. The decomposition of $C(N_5)_4$ can release an energy of 6.53 kJ g^{-1}, which, to our knowledge, is the highest recorded among room-temperature stable binary nitrogen-rich compounds. And $C(N_5)_4$ exhibits excellent detonation pressure of 44.76 GPa and detonation velocity of 10.30 km s^{-1}, which are 2 times and 1.5 times higher than those of TNT, respectively (J. Mater. Chem. A, 2024, DOI: 10.1039/d4ta01837k; Mater. Des., 2020, 193: 108820; CrystEngComm, 2020, 22(36): 6057-6062). Moreover, we proposed a series new CeN_x (x=4,5,6,7,8) energetic materials via a "high pressure catalysis" method (Matter Radiat. at Extremes, 2023, 8(3),038401).

In summary, we have proposed a new CSP method to explore the nitrogen-rich materials, opening a new avenue to explore their crystal and physical properties.

D35-P06

First Principle Study of Electronic and Optical Properties of HNS

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The electronic and optical properties of HNS have been studied using first principle method based on the density functional theory (DFT). The band structure of HNS was calculated, from which the bandgap of HNS was obtained. The complex dielectric function of HNS is obtained from the derivative of the wave function with respect to the wave vectors in three dimensions. The peaks in the spectrum curve of the complex part of the complex dielectric function are analyzed on the density of states (DOS). The relationship between peaks in the dielectric function spectrum and the band structure was analyzed. The refractive index, extinction coefficient and reflectivity of HNS are also computed from the complex dielectric function.

D35-P07

Azo Pyrazole Carboxylic Derivatives for Potential Energetic Materials

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Ideal energetic materials require the high densities, favorable thermal stability, high-energetic characteristics, low sensitivity to impact and friction, and safe environmental compatibility. Moreover, in view of the need for large-scale production, the synthesis routes for energetic materials must be as short as possible. In this study, a novel low sensitivity energetic compound 1,2-bis(3-carboxy-4-nitro-1H-pyrazol-5-yl) diazene 1-oxide (**5**) was synthesized simply and efficiently. 5-amino-3-(1H-tetrazol-5-yl)-1H-pyrazole-4-carbonitrile (**2**) was prepared by cycloaddition reaction of 5-amino-1H-pyrazole-3,4-dicarbonitrile (**1**) with sodium azide. Compounds 1 and 2 are coupled to form azo pyrazole compounds 3 and 4, followed by nitrating to obtain compounds 5 and 5,5'-(diazene-1,2-diyl) bis(3-(1H-tetrazol-5-yl)-1H-pyrazole-4-carboxylic acid) (**6**). For the sake of exploring their potential as energetic materials, elemental analysis, multinuclear NMR spectroscopy, infrared spectroscopy and single-crystal X-ray diffraction were applied to investigate the properties of such compounds. The calculated detonation properties of **4-6** (7480-8190 $m\cdot s^{-1}$) are superior to that of the traditional explosive TNT (6881 $m\cdot s^{-1}$). In addition, **4-6** have higher decomposition temperature (T_d = 212 °C - 260 °C) than RDX (T_d = 204 °C). Meanwhile，**5** and **6** also have the lower mechanical sensitivities (IS = 40 J, FS ＞ 360 N) than RDX (IS = 7.5 J, FS = 120 N). The results showed that the azo pyrazole carboxylic acid derivatives could be used as low sensitivity energetic materials.

D35-P08

Cocrystals Strategy towards Novel Laser initiation materials

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Based on the inspiration of "bimolecular hydrogen transfer" and "the detonation sequence", this study constructed a novel non-metallic laser initiation material, DA-20, which is a cocrystal of 4,4',5,5'-tranitro-1H,1'H-[2,2'-biiminidazole]-1,1'-diamine (DATNBI) and Hexanitrohexaazaaisowurtsowurtzitane (CL-20). Co-crystallization of DATNBI and CL-20 generates a “initiation sequence structure” at the molecular level, a new structure that assembles primary explosives and secondary explosives within a unit cell. Under laser induction, DATNBI acts as a “initiator,” causing to CL-20 decompose and detonate at the molecular level. Through Gaussian simulations and in-situ Fourier transform infrared (in-situ FTIR) analysis, the decomposition mechanism of DA-20 induced by hydrogen radical transfer was discovered. As far as we know, this is the first co-crystalline laser-sensitive initiation material. Furthermore, the direct initiation of CL-20 using a “initiation sequence structure” design at the molecular level is unprecedented. This approach provides important insights for the development of a new generation of non-metallic, environmentally friendly, and low-sensitivity laser initiation materials.

D35-P09

Towards Laser-Sensitive Explosives：One-Step Realization of Skeleton Editing, Geminal-Dinitro Introduction and Zwitterionization in An Energetic Molecule

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For a long time, the most widely used strategy for designing new energetic materials has been to combine energetic moieties with various skeletons within an energetic molecule.[1]Currently, the skeletal editing has been receiving increasing interest because it enables the modification of underlying molecular skeletons and provides new opportunities to synthesize complex molecules through completely different strategies.[2-5]This study proposes a one-step reaction that realizes the skeletal editing of energetic skeletons and introduces the energetic group bis(nitro)methylene while simultaneously achieving zwitterionization. By using 1-methyl-5-hydroxypyrazole as the raw material, a novel energetic molecule, 1-methyl-4-bis(nitro)methyleneoxadiazole (NPX-4), was synthesized through a promising one-step reaction. NPX-4 exhibits excellent detonation properties (D=8483 m s-1, P=31.3 GPa) and promising laser-induced detonation performance, indicating significant potential as a novel

initiating explosive. Our work demonstrates the possibility of applying skeletal editing techniques to design new energetic materials.

D35-P10

2,2,2-Trifluoroethyl-functionalized 1-methyl-3,5-dinitro-1H-pyrazol-4-amine as insensitive and thermostable energetic melt-castable material

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Energetic melt-castable materials are a category of special energetic materials with the melting points in a narrow temperature range of 70~120℃[1]. This reversible solid-to-liquid phase-changing ability make them as the irreplaceable carrier in composite explosive[2]. With the increasing attentions on high-efficiency energy release of Al-based composite explosives, fluorine-containing energetic melt-castable materials have gained more and more interests in recent ten years[3-4]. However, there were only around a dozen of fluorine-containing energetic melt-castable compounds reported so far, which indicates that the related studies are still limited. Here, we designed a new fluorine-containing parazole molecule (TFDNPA) by 2,2,2-trifluoroethyl functionalizing 3,5-dinitro-1H-pyrazol-4-amine (LLM-116) in one-step reaction. TFDNPA has suitable melting point (Tm: 100 ℃) and excellent thermal stability (Td: 309 ℃). At the same time, TFDNPA exhibits higher detonation properties (VD:7488 ms^{-1}, P: 25.45 GPa) and lower impact sensitivity (>40 J) than those of TNT (6779 ms^{-1}; 18.35 GPa and 15 J), demonstrating its potential as insensitive and thermostable energetic melt-castable material.

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D35-P11

Preparation and properties of hypergolic kerosene-based composite fuel

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Aviation kerosene is widely used as a fuel in bipropellant of liquid rocket engine due to its nontoxic, high calorific value, good combustion performance. Though aviation kerosene has a series of advantages, non-hypergolic feature is a representative shortcoming. Hypergolic bipropellant has attracted abroad attention because of no additional ignition device and more controlled ignition. To the best of our knowledge, there are no suitable additives have been found to cause aviation kerosene to self-ignition with oxidants, such as white fuming nitric acid (WFNA). Inspired with the fact that catocene can improve the burning performance of gas oil, we are envisioned that the addition of ferrocene-based compounds might cause the self-ignition of aviation kerosene with WFNA. As we expected, a ferrocene derivative (denoted as FcR) was found to cause aviation kerosene spontaneous combustion in contact with WFNA. The ignition tests show that the ignition delay time (tid) of composite fuel I (35. wt% FcR and

65. wt% aviation kerosene) is 73 ms, and the tid of composite fuel II (30. wt% FcR and 70. wt% aviation kerosene) is 90 ms (millisecond), but the kerosene isn’t ignited when the content of FcR is less than 30. wt%. Although the tid of mixture is slightly long, it indicates a possible direction for the hypergolic ignition of aviation kerosene. The introduction of reducing groups on the ferrocene skeleton may further reduce the tid between aviation kerosene and WFNA or other oxidants.

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D35-P12

Energetic Copper(II) Quadridentate Chelate: A Novel Green Laser-sensitive Primary Explosive

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Laser-sensitive primary explosives (LSPEs) have always been a focus of attention as the material foundation for safer and more efficient laser initiation technology. However, LSPEs often have poor safety due to their structural characteristics, which greatly limits the development and application of laser-initiating technology. In this work, we introduced the concept of multidentate chelates into LSPEs and innovatively proposed the concept of energetic quadridentate chelates. To achieve this highly creative idea, we synthesized an energetic flexible chelating ligand 1,2-Bis(3-nitroamino-1,2,4-triazol-5-yl)ethane (BNATE) and prepared one novel metal quadridentate chelate [Cu(BNATE)·2H2O] (1) by chelating it with Cu2+. Through a series of tests such as X-ray single crystal diffraction analysis, thermogravimetric analysis, and differential scanning calorimetry (TG-DSC), and the evaluation of safety and detonation performance, it has been proven that this compound adheres to the high stability characteristics of the chelate, and its safety and detonation performance is superior to previous LSPEs. At the same time, through laser initiation experiments, it is determined that the compound also has excellent photosensitivity and a lower laser initiation threshold. In order to explain the reason why the chelate structure is specifically sensitive to laser, diffuse reflection ultraviolet and TD-DFT simulations were conducted, which not only demonstrated experimentally that chelation has a good enhancement effect on laser photosensitivity but also confirmed the mode of electron transfer in the quadridentate chelate structure.

D35-P13

Full Positively Charged Pd Supported on Defect-Rich N-doped Hollow Carbon Nanosheets as Active Sites for Efficient Hydrogenolytic Debenzylation of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HBIW)

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Polyazacage nitroamine compounds have been one research focus on of high energy density materials, among which hexanitrohexaazaisowurtzitane (CL-20) was an outstanding representative. The effective way to synthesize the cage nitroamines is to synthesize the cage type parent derivatives firstly, and then convert the protective group on the nitrogen atom into the nitro group. Benzyl is a widely used protecting group, so the catalytic transformation of N-benzyl group is a key step in the synthesis of such kind of cage nitroamine molecules. However, due to the poor stability of the polyaza cage framework, the debenzylation catalyst with much high activity is desirable. Therefore, it is very important in theory and practical application to fabricate the hrdrogenolytic debenzylation catalyst with high efficiency for the cage substrates and reveal the relationship between the catalyst performance and its structure.

In this work, N-doped hollow carbon nanosheet assemblies (HCNAs) were first developed by hydrothermal carbonization of glucose in the presence of zinc nitrate, trisodium citrate (TC), and hexamethylenetetramine (HMT) through an in situ self-generating template method, and the corresponding Pd-based catalyst (Pd/HCNAs) fabricated by a conventional deposition-precipitation method showed superior catalytic activity and high stability for the debenzylation of HBIW under the atmospheric pressure, which was mainly attributed to its positive charged Pd active sites and the strong interaction between Pd species and the HCNAs support, benefiting from the N-doping and defect sites introduction. The results of this work may provide a strategy to design and construct efficient catalysts for the hydrogenolysis of debenzylation.

D35-P14

Preparation,Characterization of ADN/PDO Cocrystal Oxidizer and Its Compatibility With the Components of Propellants

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Ammonium dinitramide / pyrazine-1,4-dioxide (ADN/PDO)cocrystal oxidizer was prepared by ultra high efficiency mixing method. X-ray diffraction and differential scanning calorimetry were utilized to determine whether the cocrystal was prepared. The crystal morphology, particle size of cocrystal oxidizer were characterized and tested. Results indicate that prepared samples are regular block-like ADN/PDO cocrystal oxidizer with uniform particle size, which appear new stronger diffraction peaks at 15.551°, 17.218°, 19.011°, 19.264°, 24.436°, 30.954°, 35.551°. Thermal analysis of ADN/PDO was conducted by differential scanning calorimetry(DSC), ADN/PDO cocrystal begins melting at 114.2 °C an increase of >20 ^{o}C relative to ADN (92.3 ^{o}C). and the decomposition of ADN/PDO commences at 179 ^{o}C, a 19 ^{o}C higher value than ADN (160 ^{o}C). The compatibility of ADN/PDO cocrystal with components of solid propellant, including hydroxyl-terminated glycidylazide polymer(HGAP), triisocyanate(N-100), ammonium perchlorate(AP), hexanitrohexaazaisowurtzitane (CL-20), cyclotetramethylene tetranitramine(HMX), aluminum powder(Al powder) were investigated by differential scanning calorimetry(DSC). The ADN/PDO cocrystal is compatible with HGAP, N-100, AP, CL-20, HMX and Al powder.

D35-P15

High Cis-1,4 Content Epoxy-Terminated Polybutadiene Elastomers: Enhancing Low-Temperature Performance for Solid Propellant Applications

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Telechelic polybutadiene liquid rubber is a widely utilized binder for energetic composite materials such as solid rocket propellants. Conventional HTPB-isocyanate curing systems encounter significant challenges due to the high reactivity of isocyanates, which readily react with atmospheric moisture, leading to bubble formation. Furthermore, there is an increasing demand for enhanced environmental adaptability of propellants. Hence, it is

imperative to develop non-isocyanate crosslinking systems and extend the operational temperature range of polybutadiene liquid rubber. In this study, carboxyl-terminated polybutadiene (CTPB) with a high cis-1,4 structure content was synthesized via the oxidative cleavage of polybutadiene rubber. This CTPB was subsequently converted to epoxy-terminated polybutadiene (ETPB) through an acylation reaction with glycerol. The molecular structure and molecular weight of the resultant ETPB were thoroughly characterized. The results indicated that ETPB possessed a cis-1,4 structure content exceeding 96%, with molecular weights ranging from 4000 to 11000 and a polydispersity index (PDI) between 2 and 3. ETPB elastomers were fabricated by curing and crosslinking ETPB using pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), polyamide 650 (PA650), and cystamine as curing agents. Tensile strength testing revealed that with an increase in the molecular weight of ETPB, the elongation at break of the ETPB elastomers increased while the tensile strength decreased. Dynamic mechanical analysis (DMA) demonstrated that ETPB elastomers remained in a rubbery state at -100°C, highlighting their excellent low-temperature resistance.

D35-P16

Relaxation of covalent bonds in energetic material molecular crystals under pressure and temperature fields

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Energetic materials are crucial for aerospace technology, homeland security, and civil engineering construction. However, it is extremely challenging to systematically understand fundamental scientific focus issues such as structural stability, energy storage density, impact sensitivity, and detonation intensity. This study starts from the perspective of intermolecular and intramolecular coupling, and proposes and confirms the relaxation behavior of coupled hydrogen bonds in energetic material structures through perturbation spectroscopy measurements and quantum computing methods. The pressure induced elongation and temperature induced contraction caused by the coupling effect of its covalent part H-N/O; However, due to the contraction of low coordination bonds and under coupling effects, the vibration frequency of H-N/O dangling bonds not only increases but also follows the conventional compression thermal expansion law. These rules deepen our understanding of the structural stability of energetic materials.

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