Synthesis and characterization of nitrogen-rich polybenzoxazines for energetic applications

Slimane Abdous¹, Mehdi Derradji¹, Oussama Mehelli¹, Raouf Belgacemi¹, Sarah Soudjrari¹, Noureddine Ramdani¹, Karim Khiari¹, Mohamed El Amine Kadi¹ and Wenbin Liu²

Abstract
In a vision to develop new synthetic routes for the preparation of energetic materials, two new energetic benzoxazine monomers were synthesized via a two-step Mannich reaction process involving the incorporation of nitrogen–nitrogen bonds and explosophore groups (NO₂) into the monomer backbone. The molecular structures of the synthesized monomers were confirmed by ¹H NMR, Fourier transform infrared and elemental analysis techniques. The curing behavior and the degradation phenomena were evaluated by differential scanning calorimetry-thermogravimetric analysis analyses. The two monomers showed two distinct exothermic peaks related to the polymerization and degradation phases. The energetic performances were evaluated by determining the heat of combustion and formation using a bomb calorimeter, in an oxygen atmosphere. The results indicated that the 2,4 dinitrophenylhydrazine–based benzoxazine has better energetic properties than the phenylsemicarbazide-based benzoxazine, and the two developed polymers showed comparable performances with nitrocellulose and glycid azide polymer. Overall, this study has demonstrated that the ease of synthesis of the benzoxazine resins via Mannich reaction can be further extended to the energetic field and further research is undergoing to fully unravel the potential of these exceptional materials.

Keywords
Benzoxazine, Mannich reaction, energetic polymers, explosophore groups

Introduction
Hybrid propellant is a stable product at ambient temperature, composed of a liquid oxidizer and solid fuel, and it differs from the liquid propellants in which both the oxidizer and the fuel are liquids, whereas a solid propellant is composed of polymeric matrix where the oxidizing particles are dispersed, and it is widely used in tactical systems and space operations.¹-³ Hybrid propellants were tested for years to solve safety and controllability issues that are difficult to control for solid propellants.⁴,⁵ Therefore, many advantages over solid rockets can be highlighted, such as an increased power, restart ability, and power control. The use of solid propellants instead of liquids is primarily preferred because of cost and reliability; expanded weight and toxicity of the liquid oxidizer. Hybrid hypergolic system makes them possible to eliminate liquids propellants deficiencies while preserving their advantages.⁶

The combustion process of hybrid systems is based on the instant auto-ignition reaction upon the mutual contact of the liquid oxidizer with the solid combustible. Therefore, fuels that ensure self-ignition are in great demand. One of the fuels of interest in hybrid systems is borane ammonia which is a stable solid material under typical atmospheric conditions.⁷-⁸ In practice, this latter must be casted with a polymeric binder into the desired grain shape.⁹ Although the commonly used inert binders, such as hydroxyl-terminated polybutadiene and carboxy-terminated polybutadiene (CTPB), have excellent mechanical properties, they negatively

¹UER Procédés Energétiques, Ecole Militaire Polytechnique, Bordj El Bahri, Algeria
²Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Institute of Composite Materials, Harbin, China

Corresponding author:
Mehdi Derradji, UER Procédés Energétiques, Ecole Militaire Polytechnique, BP 17, Bordj El Bahri 16111, Algeria.
Email: derradjimehdi1@gmail.com
affect the overall combustion energy of energetic mixtures; such as the ignition delay (ID: the time counted from the contact between the first drop of the liquid oxidizer with solid fuel until the auto-ignition) for hypergolic systems and the specific impulse for solid systems, among others.\textsuperscript{10,11} This dilution of energetic performances can be mitigated by using energetic binders and polymers which can ensure the auto-ignition with better performances.

Nitrogen-rich polymers are relatively newcomers. Indeed, this category of polymers includes all polymers having a nitrogen–nitrogen (N–N) bond in their structures, such as hydrazine and hydrazone. The self-ignition nature of these (N–N) bonded polymers upon contact with liquid oxidizer such as white fuming nitric acid and nitrogen tetroxide is well known.\textsuperscript{12} Overall, many N-N bonded resins have been synthesized, such as di-epoxide of bis-furfuraldehydecarbono-hydrazine, di-epoxide of bis-furfuraldehydethiocarbono-hydrazine, and di-epoxide of sebacoyl bis-furfuraldehydecarbono-hydrazine, and it is reported in the literature that the use of this class of resins offers interesting advantages, whether for hybrid or solid systems. These interesting features are related to the fact that they have high densities, which in turn allow high specific impulse values compared to polybutadiene-based binders.\textsuperscript{12–14}

In the recent years, there has been an increasing interest in the N–N bonded thermosetting resins. For instance, N–N bonded epoxides have been developed for solid and hybrid propellants.\textsuperscript{15,16} Since most of the N–N bonded systems are known to be hypergolicity with the liquid oxidizer, it was predicted that N–N bonded polymers having explosophore groups (NO\textsubscript{2}) in addition to the N–N bonds in their backbone would have desirable energetic performances and low ignition delay. In the meantime, developing a safer synthetic route to incorporate explosophore groups into polymers has always been a challenging task. The Mannich reaction, consisting of the simple combination of a phenolic derivative, formaldehyde and a primary amine, offers a wide range of possibilities in the field of polymer. Indeed, a new type of thermosetting resins, namely the benzoxazine, has appeared recently and has claimed the advantage over traditional high-performance polymers. Therefore, it was brought to our attention to exploit the design flexibility of Mannich reaction monomer as a novel synthetic route for the development of a new generation of energetic polymers that beat N–N bonds and explosophore groups.

Benzoxazine is a molecule in which a hetero-cyclic six membered ring with nitrogen and oxygen atom is attached to a benzene ring, depending on the position of the nitrogen and the oxygen heteroatoms a variety of benzoxazine structures can be developed. Polybenzoxazine is novel class of phenolic-thermosetting resins, with unique properties that make them ideal alternative for applications where traditional thermosetting resins have failed. The history of benzoxazine chemistry dates since 1944 when Holly and Cope reported the synthesis of the first benzoxazine monomer.\textsuperscript{17–19} Thanks to the flexibility of molecular design, benzoxazine resins have excellent mechanical and physical properties, near-zero shrinkage, high char yield, low water uptake and good thermal, chemical and electrical properties.\textsuperscript{17–21}

In the light of the previous facts, we herein report the synthesis and characterization of two new energetic benzoxazine polymers having N–N bonds along with nitro (NO\textsubscript{2}) explosophore groups in their backbone via a two-step Mannich reaction process. The aim is to investigate the feasibility of the Mannich reaction in the development of energetic materials. Additionally, the effect of the N–N bonds and nitro groups on the curing behavior, degradation mechanism, thermal stability, heat of combustion, and self-ignition behavior are also investigated.

Experimental

Materials

Phenysemicarbazide (99.5%) and paraformaldehyde were purchased from Shanghai Aladdin Reagents (China). Para-nitrophenol (99.5%) and 2,4 dinitrophenylhydrazine (DNPH) (97%) were acquired by Sigma-Aldrich (France). The 1,4-dioxide (99.8%), acetone and chloroform (99%) solvents were supplied by Honeywell Riedel-de-Haen (Germany). The sodium hydroxide (97%) was purchased from Fisher Scientific (USA). All chemicals were used as received without further purification.

Synthesis of 2,4 DNPH and phenylsemicarbazide–based benzoxazine monomers

The nitro-based benzoxazine monomers were synthesized following the typical two-pot Mannich reaction involving phenysemicarbazide, paraformaldehyde, para-nitrophenol and 2,4 DNPH. For convenience, the 2,4 DNPH and phenylsemicarbazide–based benzoxazine monomers were labeled DNPH-Bz and SC-Bz, respectively. The detailed synthetic route for the Bz monomers is presented in Figure 1.

Typically, a mixture of phenysemicarbazide (3 g, 19.84 mmol), para-nitrophenol (2.75 g, 19.84 mmol), and a 1,4-dioxide solution was placed in a 500 mL three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, and a thermometer. The mixture was stirred at 100°C for 30 min, and then paraformaldehyde (1.191 g, 39.69 mmol) was added and reacted at 130°C for 40 min. After cooling to room temperature, the product was first washed many times with distilled water, then dissolved in 100 mL of chloroform and purified by washing with about 1 L of 1 N sodium hydroxide solution. Finally, the solvent was allowed to evaporate in a vacuum oven and the product
was recrystallized from acetone/chloroform (2/1) and dried at 110°C for another 7 h.

Crude benzoxazine as a solid yellowish color was obtained for the SC-Bz with yield of 88%. Elemental analysis: (%) calculated for C₁₅H₁₄N₄O₄ (314) C, 57.32; H, 4.46; N, 17.83; Found: C, 57.11; H, 4.32; N, 17.67. While a brownish color for DNPH-Bz was observed, with a yield of about 90%, as shown in Figure 2. Elemental analysis: (%) calculated for C₁₄H₁₁N₅O₇ (361): C, 46.54; H, 3.05; N, 19.39; found C, 46.41; H, 2.96; N, 19.28.

Preparation of the nitrogen-rich benzoxazine polymers

The cationic ring-opening polymerization of the developed nitrogen-based benzoxazine monomers was achieved without initiators or catalysts following the curing program: 160°C/3 h, 200°C/2 h that ensure best thermal properties of the polymer. Figure 3 illustrates the cationic ring-opening polymerization and the final structure of the SC-Bz and DNPH-Bz polymers. The polymerization mechanism has been investigated by several authors, so that the N and O heteroatoms act as initiator centers that lead to the formation of repetitive phenoxyl bonds, which will rearrange on phenolic structure under further heating.

The polymerization will be initiated through the cationic ring-opening mechanism, where the cleavage of the covalent bond C–O preferentially takes place because of the high polarization of the C–O covalent bond compared to the C–N one, which makes the oxygen protonated more reactive than the nitrogen protonated species. Overall, the polymerization occurs through three main steps: 1—initiation of the oxygen site by the temperature, then 2—the cleavage of C–O bond, and the formation of the active intermediate followed by 3—the aromatic electrophilic substitution which in turn leads to the formation of the phenoxyl structure; this later rearranges in phenolic structure as emphasized in Figure 4.

Characterization techniques

Proton ¹H NMR spectra were recorded with a Bruker NMR400 spectrometer (400.13 MHz) using DMSO-d₆ as solvent and tetramethyl silane as internal standard. Elemental analyses (C, H, N, O) were conducted on a Thermo Flash EA 1112-NCHSO analyzer.

Fourier transform infrared (FTIR) spectra of the monomer samples were acquired using a Perkin Elmer100 spectrometer equipped with a deuterated triglycine sulfate detector and KBr optics. Transmission spectra in the range from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹ were obtained after averaging two scans by casting a thin film on a KBr monomer plate.

The thermal behavior of all samples was assessed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC was also employed to measure the glass transition temperature (Tg) of the cured polymers. TGA experiments were carried out with a TGA analyzer.
(Perkin Elmer TGA 4000 analyzer) under a nitrogen atmosphere (100 mL/min), while DSC analyses with a DSC 2920 model from TA Instruments with a heating rate of 10°C/min and a nitrogen flow rate were recorded at 60 mL/min for all tests.

Samples densities of the SC-Bz and DNPH-Bz polymers were determined using an electronic densimeter, type Accupyc 1340 II Pycnometer (Micromeritics) via gas displacement method to measure the volume of the samples. The helium was used as displacement medium and the samples masses were initiated; several measurements were performed.

In order to evaluate the energetic properties of the various cured polymers (SC-Bz and DNPH-Bz), their heats of combustion ($\Delta U_{\text{comb}}$) were first determined with a Parr 6200 bomb calorimeter in an oxygen atmosphere. Each polymer was pressed with mass of 200–300 mg, the combustion was ensured without using benzoic acid. The obtained results represent the average of three separate measurements.

In addition, the deflagration character of the synthesized polymers was studied by the normalized deflagration tester (OZM Type: V.69179.64000) with temperature range (25–425°C) with a sample mass of 500 mg and heating rate of 5 °C/min.

**Results and discussion**

**Synthesis of nitrogen-rich benzoxazine monomers**

The $^1$H NMR spectra of the SC-Bz and DNPH-Bz are shown in Figures 5 and 6, respectively. Depending on the

![Figure 4. Proposed mechanism for the benzoxazine ring-opening polymerization.](image)

![Figure 5. $^1$H NMR spectrum of the DNPH-Bz. DNPH, dinitrophenylhydrazine.](image)
structure of monomers and surrounding groups of the oxazine ring, a shift in the proton resonance signal of the oxazine ring was observed. The characteristic proton resonances of the oxazine ring appeared as two singlets at 3.83–3.98 and 5.42–5.79 ppm, respectively, assigned to methylene $-\text{CH}_2\text{-N} -$ and methylene $-\text{O-CH}_2\text{-N} -$ of the SC-Bz. The chemical shifts at 4.67 and 5.80 ppm are attributed to the resonance of the proton atom of $\text{N} - \text{C} - \text{Ar}$ and $\text{O} - \text{C} - \text{N}$, respectively, of the oxazine ring of DNPH-Bz.26,27 The rest of the chemical shifts assignments are clarified in the Figures 5 and 6.

The FTIR spectra of the synthesized SC-Bz and DNPH-Bz monomers are shown in Figure 7. The assignment of C–O–C modes of the benzoxazines was based on literature values.28 The C–O–C antisymmetric and symmetric stretching modes appeared in the 1270–1210 and 1090–1020 cm$^{-1}$ regions, while the antisymmetric and symmetric C-N-C stretching modes can be depicted in the 1190–1020 cm$^{-1}$ and 830–740 cm$^{-1}$ intervals, respectively. The absorptions bands at 1249 and 1080 cm$^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of C–O–C, respectively.29,30 Absorption bands assigned to the antisymmetric and symmetric C–N–C appeared at 1158 and 752 cm$^{-1}$, respectively.31,32 The absorption band at 1491 cm$^{-1}$ was attributed to the bending mode in the C–H in-plane of the trisubstituted benzene ring and the bands at 944 cm$^{-1}$ was related to the out-of-plane bending vibration of the C–H group, due to the characteristic mode of benzene attached to the oxazine ring.22,31,32 The wide band in the region of 3100–3500 cm$^{-1}$ was assigned to the symmetric and asymmetric stretching of both N–H and O–H.

Figure 6. $^1$H NMR spectrum of the SC-Bz.

Figure 7. Fourier transform infrared spectra of the synthesized nitrogen-rich benoxazines monomers.
The two absorption bands at 1343 and 1565 cm\(^{-1}\) were assigned to the stretching vibration of the –NO\(_2\) group.\(^{22,35}\)

### Curing behavior

Differential scanning calorimetry tests were performed to study the curing behavior of the newly developed SC-Bz and DNPH-Bz monomers. The obtained curves are shown in Figure 8 and the thermal properties are summarized in Table 1. Differential scanning calorimetry investigations of these monomers revealed two exothermic peaks; the first peak was attributed to the polymerization, while the second one was ascribed to the degradation of the two resulting polymers. In the DSC curve of the DNPH-Bz, the exothermic peak associated with the ring-opening polymerization of benzoxazine was observed at an onset temperature (the onset of a transition event is where the tangent line intersects the baseline) of about 151.2°C. This latter was delayed, in the case of SC-Bz, where the onset polymerization’s peak was observed at around 188.7°C. This phenomenon is due to the catalytic effect caused by the presence of explosophore groups in the DNPH-Bz comparing to the SC-Bz monomer. Furthermore, the second exothermic peak maxima were detected at approximately 278.6°C and 281.5°C for DNPH-Bz and SC-Bz, respectively. Moreover, as reported in Table 1, the polymerization enthalpy per unit of mass for the SC-Bz is much lower than that of the DNPH-Bz. This behavior could be explained by the presence of a greater number of explosophore groups in the DNPH-Bz (three explosophore groups per monomer) in contrast with the SC-Bz (one explosophore group per monomer).

### Calorific power

To analyze the energetic properties of these newly developed polymers, the heats of combustion (\(\Delta U_c\)) of all the samples were experimentally determined by bomb calorimetry and the obtained data are summarized in Table 2. Meanwhile, by further applying the Hess’s law, the enthalpy of formation (\(\Delta H_f\)) was also deduced, as reported in the literature.\(^{36}\) Considering the heats of formation of H\(_2\)O (l) and CO\(_2\) (g) of –286 kJ·mol\(^{-1}\) and –394 kJ·mol\(^{-1}\), respectively.\(^{37}\) The combustion reactions of the two samples are shown in Figures 8 and 9.

Combustion is an exothermic reaction; therefore (\(\Delta H_c\)) is always negative. This parameter corresponds to the energy released when the chemical bond is broken during the reaction, and forms the combustion product of the starting compound.\(^{38}\)

It has clearly been seen that the heat released during the combustion reaction of the SC-Bz polymer was much higher than that of the DNPH-Bz. These results also revealed that the experimentally determined molar enthalpy of combustion of both DNPH-Bz and SC-Bz was greater than that of the nitrocellulose and GAP polymers. In addition, these polymers have a promising feature, which in turn,
constitute one of the basic requirements for achieving higher Isp values. Furthermore, both of the DNPH-Bz and SC-Bz have a low negative heat of formation. It is important to point out that when a molecule has a negative heat of formation, it means that this molecule releases an amount of energy during its formation reaction from basic elements, and therefore the product is more stable than the basic reagents used to form it (C₆H₄N₄O₈ in this case). Nonetheless, if the monomer has a positive (ΔHf), this means that the initial reagents are more stable than the final product and the product requires energy to be formed. Thus, due to the negative enthalpy of formation of DNPH-Bz and SC-Bz certain stability may also be associated with these nitrogen-rich monomers. Indeed, among the basic requirements in the propulsion field, the fuels and oxidizers should have positive or low negative heats of formation, and the developed polymers, with their low negative heats of formation, fulfill this condition. The molar enthalpy of formation (ΔHf) is obtained with the following equation:

\[
\Delta H_f (\text{polymer}) = a \Delta H_f (\text{CO}_2) + b \Delta H_f (\text{H}_2\text{O}) - \Delta H_f (\text{polymer})
\]

1) \( \text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_4 + 16.5\text{O}_2 \rightarrow 15\text{CO}_2 + 7\text{H}_2\text{O} + 2\text{N}_2 \)

2) \( \text{C}_{14}\text{H}_{11}\text{N}_5\text{O}_7 + 13.25\text{O}_2 \rightarrow 14\text{CO}_2 + 5.5\text{H}_2\text{O} + 2.5\text{N}_2 \)

**Density:** The density of energetic materials is one of the most physical properties, since it affects the loading density. The density of DNPH-Bz was found to be much higher than that of SC-Bz, and it should be noted that the densities of this N–N bonded polymers are in the range of commonly used polymers, such as the GAP-diol, and much higher than others like CTPB (ρ = 0.92 g.cm⁻¹), because the introduction of N elements and nitro groups make the densities increase by 0.12–0.2 g.cm⁻¹. Glass transition temperature: In simple terms, the Tg is a secondary order transition temperature that represent a discontinuity in the second derivative of Gibbs free energy (ΔG). And it is the temperature at which materials shift between glassy and rubbery physical states. Numerous methods have been developed to measure the Tg, such as dynamic mechanical analysis, differential scanning calorimetry and dielectric spectroscopy. Differential scanning calorimetry is the most commonly analytical technique used for measuring the Tg of polymers, and it was used in this study (Figure 10) to quantify this important transition for these newly developed polymers.

**Oxygen balance:** Oxygen balance is defined as the amount of oxygen in default or in excess with regard to what is required for a completed combustion, and it is important

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### Table 2. Physical and Energetic Data of the Nitrogen-Rich Benzoxazine Polymers.

| Sample | DNPH-Bz | SC-Bz | GAP-DIOL | NC |
|--------|---------|-------|----------|----|
| Formula (repeating unit) | \( \text{C}_{12}\text{H}_{11}\text{N}_4\text{O}_7 \) | \( \text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_4 \) | \( \text{C}_8\text{H}_{14}\text{N}_6\text{O}_4 \) | \( \text{C}_6\text{H}_7\text{O}_2(\text{OH})_{0.7}(\text{ONO}_2)_{2.3} \) |
| Molecular mass (g.mol⁻¹) | 361 | 314 | 258 | 265.5 |
| Appearance | Yellow powder | Brown powder | Light yellow liquid | White fibers |
| \( T^a \text{ Dec (°C)} \) | 278.6 | 281 | 202.03 | 176.78–263.03 |
| \(-\Delta U_{comb} (kJ.g⁻¹)\b | 19.441 | 24.726 | 1.910 | 10.27 |
| \(-\Delta H_{comb} (kJ.mol⁻¹)\c | 7010.15 | 7762.73 | 474.462 | 2716.7 |
| \(-\Delta fH (kJ.mol⁻¹)\d | 78.85 | 149.27 | 301.86 | 652.6 |
| OB\* (%) | -117.45 | -168 | -117.83 | -37.66 |
| \( T_{\text{def}} (°C) \) | 245 | 257 | - | 185.4 |
| \( \rho (g.cm⁻³) \) | 2.603 | 1.576 | 1.29 | 1.673 |
| \( T_{\text{b}(g)} (°C) \) | 179 | 167 | -45 | 68 |

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*a, Temperature of decomposition determined by DSC (β = 10°C/min, onset values); b, experimental combustion energy (constant volume); c, experimental molar enthalpy of combustion; d, molar enthalpy of formation; e, oxygen balance calculated from the equation (\( d - 2a - b/2 \))1600/\( M \); f, deflagration temperature determined by means of deflagration temperature determination device; g, density derived from pycnometer measurement; h, glass transition temperature; i, characteristics of glycid azide polymer-DIOL; j, physical and energetic properties of nitrocellulose with a different nitrogen content and humectants with isopropanol; k, decomposition temperature of NC with different alcohol humectants.
indicator to determine the potential of an energetic material mostly explosives and oxidants, which require a positive oxygen balance, but the default in oxygen balance in these latter could be covered by binders or fuel that have excess of oxygen in their formulations. As seen in Table 2, the oxygen balance of DNPH-Bz is superior to that of SC-Bz and almost akin to that of GAP-diol. What is more, the oxygen balance of the synthesized polymers could be enhanced by the nitration of the polymer backbone without amending the neither the sensibility nor the stability of the modified polymer.

**Auto-inflammation temperature (or deflagration temperature):** To further evaluate the nitrogen-rich polymers, auto-inflammation temperature was measured using standard procedures, this latter represents the response of the energetic material towards a continuous heating in metal block. Relay on the results of Table 2, the synthesized monomers have approximately closed auto-inflammation temperatures and not much higher than that of NC.

**Thermal stability**

For a better understanding, the degradation process was investigated by TGA under an N₂ atmosphere and the TGA-DTG curves of these polymers are shown in Figures 10 and 11, respectively. For both polymers, a single-step decomposition was observed at temperature range of 240–670°C for DNPH-PBz, and 190–670°C for SC-PBz, respectively. The thermal properties are summarized in Table 3. The decomposition temperatures at 5% mass loss (T₅%) and 10% mass loss (T₁₀%) were, respectively, 270.43 and 289.55°C for DNPH-PBz. Meanwhile, for SC-PBz the T₅% and T₁₀% were measured to be about 268.05 and 309.11°C, respectively. The char yield of DNPH-PBz at 800°C was about 15.65%, which is lower than the char yield of SC-PBz which was about 21.71%.

**Conclusions**

In this work, a new strategy was developed to produce new promising nitrogen-rich energetic polymers based on the Mannich reaction. The developed N–N bonded polymers were obtained after cationic polymerization of the benzoxazine monomers via the opening of the oxazine ring. In order to confirm the identity of these polymers and to underline the thermal stability, the thermomechanical properties, as well as the energetic performance, characterizations were carried out with FTIR, ¹H NMR, DSC, ATG, adiabatic calorimetry, and the normalized deflagration tests. The two N-N bonded polymers showed good thermal stability: their decomposition temperatures are significantly higher than those of GAP-diol and NC. In addition, the energy performance of the two studied polymers was shown to be significantly superior to those of GAP-diol and NC. Moreover, the developed polymers showed high densities. The deflagration temperatures of the two polymers were significantly higher than those of GAP-diol and NC. In summary, the results confirmed that the nitrogen-rich...
benzoxazine monomers and polymers can be seen as promising candidate for future applications in solid and hybrid propulsion fields.

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ORCID iDs
Mehdi Derradji @ https://orcid.org/0000-0001-5765-7992
Oussama Mehelli @ https://orcid.org/0000-0002-1381-3225
Wenbin Liu @ https://orcid.org/0000-0003-0390-8455

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