Supplementary materials

for

Synthesis and characterization of three pyrazolate inner diazonium salts: green, powerful and stable primary explosives

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### Crystal data

Table S1. Selected bond lengths (Å) and bond angles (°) in crystal for 3,5-dichloro-4-diazopyrazole zwitterion (1), 4-diazo-3,5-dinitropyrazole zwitterion (2)[2(a)], and 4-diazo-5-nitro-pyrazol-3-one zwitterion (3)

<table>
<thead>
<tr>
<th>Bonds</th>
<th>1 (Å)</th>
<th>Bonds</th>
<th>2 (Å)</th>
<th>2’(Å)</th>
<th>Bonds</th>
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<td>N3–N4</td>
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<table>
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<th>Bond angles</th>
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<th>2’ (°)</th>
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<td>111.3(1)</td>
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<td>128.90(11)</td>
<td>N3–C2–C3</td>
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<td>128.73(11)</td>
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<td>C3–C2–C1</td>
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<td>C1–C2–C3</td>
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<td>102.28(10)</td>
<td>C1–C2–C3</td>
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<td>N2–C3–C2</td>
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<td>N1–C1–C1</td>
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<td>N1–C1–N5</td>
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<td>125.83(12)</td>
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<td>126.25(11)</td>
<td>126.09(11)</td>
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<td>N2–C3–N6</td>
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<tr>
<td>C2–C3–Cl2</td>
<td>126.31(12)</td>
<td>C2–C3–N6</td>
<td>127.27(11)</td>
<td>125.95(11)</td>
<td>C2–C1–N5</td>
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<tr>
<td>O4–N6–O3</td>
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<td>O4–N6–C3</td>
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<td>O1–N5–C1</td>
<td>116.27(10)</td>
<td>O1–N5–C1</td>
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</table>

[a] For compound 2, and there are two different molecular structures in crystal, of which the crystal data are slightly distinct.
Table S2. Crystallographic data for 1, 2, and 3.

<table>
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<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
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<td><strong>Empirical formula</strong></td>
<td>C₃Cl₂N₄</td>
<td>C₃N₆O₄</td>
<td>C₃H₃N₅O₃</td>
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<td><strong>CCDC number</strong></td>
<td>1018388</td>
<td>1018387</td>
<td>1018389</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>153(2)</td>
<td>153(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td><strong>Formula weight/(g/mol)</strong></td>
<td>162.97</td>
<td>184.09</td>
<td>155.09</td>
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<tr>
<td><strong>Wavelength/Å</strong></td>
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<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td><strong>Crystal system</strong></td>
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<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>Pbca</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
</tr>
<tr>
<td><strong>a /Å</strong></td>
<td>8.814(3)</td>
<td>11.382(3)</td>
<td>5.536(7)</td>
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<tr>
<td><strong>b /Å</strong></td>
<td>9.208(3)</td>
<td>10.234(2)</td>
<td>9.134(7)</td>
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<tr>
<td><strong>c /Å</strong></td>
<td>14.261(4)</td>
<td>12.054(3)</td>
<td>11.526(8)</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β /°</strong></td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>γ /°</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>V /Å³</strong></td>
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<td>582.47(7)</td>
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<td><strong>Z</strong></td>
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<td>8</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ / (g·cm⁻³)</strong></td>
<td>1.894</td>
<td>1.849</td>
<td>1.769</td>
</tr>
<tr>
<td><strong>μ /mm⁻¹</strong></td>
<td>1.016</td>
<td>0.171</td>
<td>0.158</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>656.0</td>
<td>736.0</td>
<td>312.0</td>
</tr>
<tr>
<td><strong>Crystal size/mm</strong></td>
<td>0.48 × 0.46 × 0.31</td>
<td>0.50 × 0.42 × 0.28</td>
<td>0.24 × 0.22 × 0.22</td>
</tr>
<tr>
<td><strong>θ /°</strong></td>
<td>3.50~31.48</td>
<td>2.68~29.13</td>
<td>4.43~25.58</td>
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<tr>
<td><strong>Reflections Collected</strong></td>
<td>10549</td>
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</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>1914</td>
<td>3539</td>
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<td><strong>Rint</strong></td>
<td>0.0319</td>
<td>0.0338</td>
<td>0.0297</td>
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<tr>
<td><strong>Final R indices [I &gt; 2σ (I)]</strong></td>
<td>R₁ = 0.0370, wR₂ = 0.0997</td>
<td>R₁ = 0.0368, wR₂ = 0.0949</td>
<td>R₁ = 0.0456, wR₂ = 0.0985</td>
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<tr>
<td><strong>Final R indices (all data)</strong></td>
<td>R₁ = 0.396, wR₂ = 0.1023</td>
<td>R₁ = 0.0463, wR₂ = 0.1018</td>
<td>R₁ = 0.0749, wR₂ = 0.1135</td>
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</tbody>
</table>

Heat of formation

Isodesmic reaction, in which numbers of electron pairs and chemical bond types are conserved, has been employed very successfully to give heat of formation¹. Based on the optimized structures, the total energy (E₀) and thermodynamic parameters, including zero point energy (ZPE) and thermal correction to enthalpy (HT), were obtained at the B3LYP/6-311G+(d,p) level. For the isodesmic reaction (Scheme S1), gas-phase heat of reaction (ΔH₂⁹⁸K) can be calculated from the following Equation (1):

\[
ΔH₂⁹⁸K = \sum ΔH_{f,R}(gas,298K) - \sum ΔH_{f,P}(gas,298K)
\]  (1)

where \(H_{f,R}\) and \(H_{f,P}\) are the gas–phase heats of formation for reactants and products at 298 K, respectively.

Meanwhile, \(ΔH²⁹⁸K\) can also be calculated using the following Equation (2):

\[
ΔH²⁹⁸K = ΔE²⁹⁸K + Δ(PV) = ΔE₀ + ΔZPE + ΔHT + Δ(nRT)
\]  (2)

Where \(ΔE₀\) is the change in total energy between the products and the reactants at 0 K; \(ΔZPE\) is
the difference between the zero-point energies of the products and the reactants; ∆HT is thermal correction from 0 K to 298.15 K. Since there is no change in number of total molecules, ∆(PV) = ∆(nRT) = 0. Therefore, the heat of formation in gas-phase can be figured out according to ∆H_{298 K} and gas-phase heats of formation of other reactants and products. Fortunately, these data can be acquired from the literature and handbook facilely.

**Scheme S1. Isodesmic reactions**

![Scheme S1. Isodesmic reactions](image)

**Table S3.** Calculated total energy (E₀), zero-point energy (ZPE), thermal correction (HT), and enthalpy of formation (HOF_{Gas}) of compounds 1–3 and reference compounds.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>E₀/a.u.</th>
<th>ZPE (kJ/mol)</th>
<th>HT (kJ/mol)</th>
<th>HOF_{Gas} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H–pyrazole²</td>
<td>−226.265995</td>
<td>186.35</td>
<td>12.32</td>
<td>177.4</td>
</tr>
<tr>
<td>Methylamine³</td>
<td>−95.893889</td>
<td>167.46</td>
<td>11.52</td>
<td>−23.5</td>
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<tr>
<td>Nitromethane⁴</td>
<td>−245.091646</td>
<td>130.18</td>
<td>14.04</td>
<td>−81</td>
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<tr>
<td>Methane⁵</td>
<td>−40.533958</td>
<td>116.97</td>
<td>10.01</td>
<td>−74.6</td>
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<tr>
<td>Diazomethane⁶</td>
<td>−148.785743</td>
<td>83.10</td>
<td>11.91</td>
<td>206</td>
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<td>Chloromethane</td>
<td>−500.151876</td>
<td>98.87</td>
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<td>Ammonia⁷</td>
<td>−56.582722</td>
<td>89.96</td>
<td>10.02</td>
<td>−40.90</td>
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<tr>
<td>1</td>
<td>−1253.746877</td>
<td>97.17</td>
<td>22.54</td>
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<tr>
<td>2</td>
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<td>158.44</td>
<td>29.85</td>
<td>496.60</td>
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<tr>
<td>3</td>
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<td>167.34</td>
<td>25.63</td>
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<td>4⁸</td>
<td>−652.0221153</td>
<td>240.99</td>
<td>30.67</td>
<td>177.0</td>
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For assessment of the potential performance of the energetic material of interest, however, the desired quantity is usually the condensed phase ∆H. Condensed phase heats of formation can be determined using the gas-phase heats of formation and heat of phase transition (either sublimation or vaporization) according to Hess’ law of constant heat summation. For compounds discussed in this paper, they are all solid at room temperature and their solid heat of formation can be calculated by Equation (3). The calculation of ∆H(Sublimation) can use the method proposed by Politzer and coworkers⁹ shown as Equation (4).

\[
\Delta H(\text{Solid}) = \Delta H(\text{Gas}) - \Delta H(\text{Sublimation})
\]

\[
\Delta H(\text{Sublimation}) = a(SA)^2 + b\sqrt{\sigma_{\text{tot}}^2} + c
\]

where SA is the surface area of the 0.001 electron/bohr³ isosurface of the electron density of the molecule, σ_{\text{tot}} is a measure of the variability of electronic potential on the surface, and v is the...
degree of balance between the positive and negative charges on the isosurface. The above three parameters can be calculated by Multiwfn (version 3.3.8).\textsuperscript{10, 11} a, b, and c are constants and their value are 0.000267, 1.650087, and 2.966078, respectively.\textsuperscript{12}

<table>
<thead>
<tr>
<th>Compounds</th>
<th>SA/Å(^2)</th>
<th>(\sigma^2_{\text{tot}}/\text{(kcal\cdot mol)}^2)</th>
<th>(\nu)</th>
<th>(\Delta H(\text{Sublimation})/\text{kJ\cdot mol}^{-1})</th>
<th>HOF(_{\text{Gas}})/kJ\cdot mol(^{-1})</th>
<th>(\Delta H(\text{Solid})/\text{kJ\cdot mol}^{-1})</th>
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<tr>
<td>1</td>
<td>164.34</td>
<td>233.39</td>
<td>0.2400</td>
<td>94.30</td>
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<td>2</td>
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<td>206.42</td>
<td>0.1688</td>
<td>88.84</td>
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<td>3</td>
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<td>189.79</td>
<td>0.2028</td>
<td>84.60</td>
<td>169.77</td>
<td>85.17</td>
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**Table S4.** Calculated solid heat of formation of 1–3

**Thermal stability**

The DSC and TG spectra of compounds 1–3 are shown in Figure S1, and the thermal decomposition temperatures of some other aromatic diazonium salts and heterocyclic diazo compounds are listed in Table S5. As shown in the table, the decomposition temperatures for common diazonium salts mostly are not more than 100 °C, while the inner diazonium salts show decomposition temperatures more than 120 °C.

**Figure S1.** DSC and TG spectra of 1(a), 2(b) and 3(c).
<table>
<thead>
<tr>
<th>Compound name</th>
<th>Structure formula</th>
<th>Decomposition temperature/°C</th>
<th>Reference</th>
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<tr>
<td>Benzenediazonium chloride</td>
<td><img src="image1" alt="Structure" /></td>
<td>40 (10K/min)</td>
<td><em>R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201–211</em></td>
</tr>
<tr>
<td>2-nitrobenzenediazonium chloride</td>
<td><img src="image2" alt="Structure" /></td>
<td>60 (10K/min)</td>
<td><em>R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211</em></td>
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<tr>
<td>3-chlorobenzene diazonium chloride</td>
<td><img src="image3" alt="Structure" /></td>
<td>120 (10K/min)</td>
<td><em>R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211</em></td>
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<tr>
<td>3-nitrobenzenediazonium chloride</td>
<td><img src="image4" alt="Structure" /></td>
<td>90 (20K/min)</td>
<td><em>R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211</em></td>
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<tr>
<td>2-methyl-5-nitrobenzenediazonium chloride</td>
<td><img src="image5" alt="Structure" /></td>
<td>80 (20K/min)</td>
<td><em>R. Ullrich, T. Grewer, Thermochimica Acta 1993, 225, 201-211</em></td>
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<tr>
<td>2-diazo-4,6-dinitrophenol</td>
<td><img src="image6" alt="Structure" /></td>
<td>142(5K/min)</td>
<td><em>Kaiser M, Ticmanis U, Thermochimica acta, 1995, 250(1): 137-149</em></td>
</tr>
<tr>
<td>Chemical Structure</td>
<td>Description</td>
<td>References</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>-------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>3-benzoyl-4-diazo-5-phenylpyrazole</td>
<td>Ph-</td>
<td>N₂⁺</td>
<td>COPh</td>
</tr>
<tr>
<td>N-Methyl-3-nitro-4-diazo-5-oxo pyrazole</td>
<td>O₂N-</td>
<td>N₂⁺</td>
<td>CH₃-</td>
</tr>
<tr>
<td>4-diazonium-1,2,3-triazole-5-carboxamide</td>
<td>NH₂-</td>
<td>N₂⁺</td>
<td></td>
</tr>
<tr>
<td>5-Diazoimidazole-4-carboxamide</td>
<td>NH₂-</td>
<td>N₂⁺</td>
<td></td>
</tr>
<tr>
<td>4-diazonium-1,2,3-triazole-5-(phenyl)methane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Carboxymethyl-3-diazonio-5-nitriliminino-1,2,4-triazole dihydrate</td>
<td>N₂⁺</td>
<td>NO₂⁻</td>
<td>2H₂O-</td>
</tr>
<tr>
<td>1,10-B_{10}H_{8}(N₂)₂</td>
<td>1,10-B_{10}H_{8}(N₂)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,10-B_{10}Cl_{8}(N₂)₂</td>
<td>1,10-B_{10}Cl_{8}(N₂)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,10-B_{10}I_{8}(N₂)₂</td>
<td>1,10-B_{10}I_{8}(N₂)₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**References**

Figure S2. IR spectrum of 1

Figure S3. IR spectrum of 2
Figure S4. IR spectrum of 3

Figure S5. UV/Vis spectra for three compounds
Figure S6. $^{13}$C NMR spectrum (100 MHz) of 1 in Acetone-d$_6$ at 25 °C.

Figure S7. ESI-MS spectrum of 1.
Figure S8. $^{13}$C NMR spectrum (100 MHz) of 2 in Acetone-$d_6$ at 25 °C.
Figure S9. EI-MS spectrum of 2.

Figure S10. EI-MS spectrum of 3.
Figure S11. $^{13}$C NMR spectrum (100 MHz) of 3 in Acetone-$d_6$ at 25 °C.

Compatibility for compounds 1, 2, and 3

Energetic materials are rarely used alone, and the incompatibility between energetic materials and other components may change the thermal stability for the energetic material itself and then accelerate aging. Therefore, the compatibility of new explosive should be investigated before practical application. Differential scanning calorimetry (DSC) has been widely used in compatibility tests for energetic materials.$^{13, 14}$ The compatibilities of three target compounds with RDX and CL-20 were studied using DSC, and the DSC curves of the single and mixture systems measured at
the heating rate of $5^\circ \text{C} \text{ min}^{-1}$ are shown in Figure S12. The evaluation standards of compatibility for explosives and contacted materials are listed in Table S6.$^{15}$

**Table S6.** Evaluation standards of the compatibility for explosives and contacted materials

<table>
<thead>
<tr>
<th>Criteria $\Delta T_p$ ($^\circ \text{C}$)</th>
<th>Rating</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤2</td>
<td>A. Compatible or good compatibility</td>
<td>Safe for use in any explosive design</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Safe for use in testing when the device will be used in a very short period of time; not to be used as a binder material or when long-term storage is desired</td>
</tr>
<tr>
<td>3–5</td>
<td>B. Slightly sensitized or fair compatibility</td>
<td>Not recommended for use with explosive items</td>
</tr>
<tr>
<td>6–15</td>
<td>C. Sensitized or poor compatibility</td>
<td>Hazardous. Do not use under any conditions</td>
</tr>
<tr>
<td>&gt;15</td>
<td>D. Hazardous or poor compatibility</td>
<td></td>
</tr>
</tbody>
</table>

(a) [Graph showing DSC data for compound 1 and compound 1/RDX]

(b) [Graph showing DSC data for compound 2 and compound 2/RDX]

(c) [Graph showing DSC data for compound 3 and compound 3/RDX]

(d) [Graph showing DSC data for compound 1 and compound 1/CL-20]
The first peak temperatures and the calculated difference between the single system and the mixture system are shown in Table S7. According to Table S7, the rating for the binary systems RDX/1, RDX/2, and RDX/3 are C or D, which shows that they have poor compatibility. The results also indicate that compounds 1 and 3 both have poor compatibilities with CL-20, while compound 2 show fair compatibility with CL-20.

**Table S7.** Data of binary systems obtained by DSC

<table>
<thead>
<tr>
<th>System</th>
<th>Peak temperature</th>
<th>Mixture system a</th>
<th>Single system b</th>
<th>$T_{p1}$ (°C)c</th>
<th>$T_{p2}$ (°C)d</th>
<th>$\Delta T_p$ (°C)e</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX/1</td>
<td></td>
<td>1</td>
<td>143</td>
<td>124.0</td>
<td>19.0</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>RDX/2</td>
<td></td>
<td>2</td>
<td>155</td>
<td>134.6</td>
<td>11.4</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>RDX/3</td>
<td></td>
<td>3</td>
<td>153</td>
<td>143.6</td>
<td>9.4</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>CL-20/1</td>
<td></td>
<td>1</td>
<td>143</td>
<td>117.3</td>
<td>25.7</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>CL-20/2</td>
<td></td>
<td>2</td>
<td>155</td>
<td>150.0</td>
<td>5.0</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>CL-20/3</td>
<td></td>
<td>3</td>
<td>153</td>
<td>141.7</td>
<td>11.3</td>
<td>C</td>
<td></td>
</tr>
</tbody>
</table>

a Mixture system; 50/50-target compounds/energetic component binary system.
b Single system; the component with an exothermic peak temperature lower than another one in a two-component system.
c $T_{p1}$, the maximum exothermic peak temperature of a single system.
d $T_{p2}$, the maximum exothermic peak temperature of the mixture system.
e $\Delta T_p = T_{p1} - T_{p2}$

**Hydrolysis of three compounds**

The hydrolysis of three compounds were studied in different solutions of various pH. They are all compatible with neutral water. Compounds 2 and 3 decompose in alkaline solutions with pH > 9, which is monitored by Thin layer chromatography (TLC); however, compounds 1 could stably exist
under condition with pH = 8, 9, and 10.

**Prices of compounds 1, 2, and 3**

The overall synthesis route to three target compounds is outlined in Scheme S2. 4-Chloropyrazole is an important chemical intermediates and can be bought from most Chemical Companies with low cost. (e.g. 1500 RMB/100 g, Pure chemistry Scientific Inc.). Other chemical reagents in the reactions are also most commonly used and economically priced. Based on the chemical reagent prices, labor costs, and energy costs, the prices for three compounds are initially estimated to be 100 RMB/g.

Scheme S2. Synthesis of compounds 1, 2 and 3

**Crystal morphologies for compounds 1, 2, and 3**

Crystal morphologies images for compounds 1 (a), 2 (b), and 3 (c) were carried out using an Olympus BX43 microscope and photographed using a digital camera Canon EOS 600D camera. As seen in Figure S13, micrograph for compound 1 shows that it is needle-shaped crystals, while those of compounds 2 and 3 indicate that they are bulk crystals.

![Crystal morphologies](image)

**Figure S13.** Crystal morphologies for compounds 1 (a), 2 (b), and 3 (c)

**References**