Investigation of CL-20/TFAZ cocrystal: preparation, structure and performance

N Liu\textsuperscript{1,2}, B H Duan\textsuperscript{1}, X M Lu\textsuperscript{1,2} and B Z Wang\textsuperscript{1,2}

\textsuperscript{1} Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
\textsuperscript{2} State Key Laboratory of Fluorine & Nitrogen Chemicals, Xi’an 710065, China

Email: flackliu@sina.com

Abstract. The cocrystals of hexanitrohexaazaisowurtzitane (CL-20) and 7H-trifurazano[3,4-b:3′,4′-f:3″,4″-d]azepine (TFAZ) in a 1 : 1 molar ratio were prepared by both slow evaporation and self-assembly method. Structure determination showed that it belongs to the monoclinic system (space group P2\(_1\)) with crystal density of 1.932 g cm\(^{-3}\). The intermolecular hydrogen bonds and N–O\(\cdots\)NO\(_2\) type interactions are demonstrated as the predominant driving force in cocrystal formation. Furthermore, the cocrystals were successfully synthesized by a self-assembly method using only water as solvent at mild conditions, and the product yield was up to 92.3%. The two types of cocrystals were fully characterized by powder X-ray diffraction and scanning electron microscope. Moreover, the thermal behavior, sensitivity, and calculated detonation performances of the cocrystal were evaluated. The cocrystal exhibits good thermal stability (Td = 242.8 °C), low impact sensitivity (H\(_{50}\) = 42 cm) and friction sensitivity (P\(_f\) = 38%), high crystal density, and high calculated detonation velocity (9103 m/s). This work opens up a new perspective in the environment-friendly preparation of energetic cocrystals on a large-scale, as well as provides a potential low-sensitivity and high-energy explosive.

1. Introduction

The pursuit of high energetic performance along with good thermal stability and acceptable sensitivity is a challenging and long-standing goal for researchers in the development of high-energy density materials (HEDMs).\textsuperscript{1} Due to the high detonation properties and acceptable mechanical sensitivity, nitramine compounds hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are usually utilized as the benchmark energetic materials (EMs).\textsuperscript{2} In the last two decades, 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20) attracts considerable interests in the worldwide as a highly promising explosive.\textsuperscript{3} Compared with RDX and HMX, CL-20 exhibits higher density and detonation properties; nevertheless, the relatively high impact and friction sensitivities result in the limiting of extensive applications of CL-20. As a consequence, considerable efforts have been made to fine tune the sensitivity of CL-20 without negatively impacting the energetic performance.

Cocrystallization technology by combinition of CL-20 and insensitive coformers has been explored to resolve the conflict in recent years.\textsuperscript{4} Cocrystals can be thought of a certain crystalline substance composed of two or more neutral species via non-covalent interactions (hydrogen bonds, p–π stacking, π–π stacking or van der Waals forces).\textsuperscript{5} The increased degree of C(N)–H⋯nitro and nitro/nitro interactions between CL-20 and coformer molecules is hypothesized to improve the stability of N–NO\(_2\) bond in CL-20, thereby lowering the resulting sensitivity response to stimuli.\textsuperscript{6} There have been several examples of CL-20/EMs cocrystals investigated in past ten years.\textsuperscript{7,11} However,
except for CL-20/HMX cocrystal, most of CL-20/EMs cocrystals have been found to possess the worse relative energetic properties (density less than 1.90 g cm\(^{-3}\) and detonation velocity less than 9000 m s\(^{-1}\)) than that of HMX. Besides, most of the methods reported for the preparation of energetic cocrystals depend on the use of organic solvents or additives.\textsuperscript{12-14} Recently, we fabricated a novel energetic cocrystal of 2:1 CL-20/2,4-dinitro-2,4-diazapentane (DNDAP) through spray drying method and self-assembly method respectively, which has high crystal density (1.871 g cm\(^{-3}\)), high detonation velocity (8997 m s\(^{-1}\)) and a relatively low mechanical sensitivity.\textsuperscript{15-18} Nevertheless, large amount of organic solvents (acetone and 2-propanol) used in above methods will lead to potential environmental pollution. As both the comprehensive performance and green preparation condition of explosives permit, new coformers and environmental approach for CL-20/EMs cocrystal are still highly sought.

As a macrocyclic furazan compound, 7H-trifurazano[3,4-b:3',4'-f:3'',4''-d]azepine (TFAZ) possesses high density (1.87 g cm\(^{-3}\)) and relative high detonation velocity (8416 m s\(^{-1}\)), meanwhile the layered \(\pi\)-stacking in TFAZ crystal can play a buffer role against external stimuli and produce decreased sensitivity.\textsuperscript{19} Owing to the inexistence of nitro group in TFAZ molecule, there is weak intermolecular hydrogen bond interactions, which make TFAZ suitable donors for forming cocrystal with CL-20. The crystal structure of CL-20/TFAZ cocrystal was firstly reported by Aldoshin \textit{et al.},\textsuperscript{20} however, its spectroscopy data and physicochemical properties were not available in this literature. Herein, we prepared CL-20/TFAZ cocrystal in a 1 : 1 molar ratio by using both slow evaporation at room temperature (cocrystal 1a) and self-assembly strategy in pure water (cocrystal 1b). The chemical structures of CL-20 and TFAZ are shown in Figure 1. The crystal structure were measured by single crystal X-ray diffraction (SC-XRD) and further analyzed by performing Hirshfeld surface. Furthermore, the target cocrystals were confirmed by powder X-ray diffraction (P-XRD) and infrared spectroscopy (IR). In addition, the crystal morphology, size distribution, thermal decomposition analysis, sensitivity values, and calculated detonation properties of the CL-20/TFAZ cocrystals were also examined to find the application potential for explosive.

![Figure 1. Chemical structures of CL-20 and TFAZ.](image)

2. Experimental section

2.1. Cocrystallization method

Cocrystallization method of 1a: \(\varepsilon\)-CL-20 and TFAZ in a mass ratio of 3 : 1 were added in minimum amount of anhydrous isopropyl acetate, then the mixture was stirred at 50 \(^\circ\)C until the solids completely dissolved. The solution was passed through a 0.45 \(\mu\)m PTFE filter and evaporated over a period of 5 days at 20\(^\circ\)C, the needle-shaped colorless cocrystal 1a was obtained.

Cocrystallization method of 1b: \(\varepsilon\)-CL-20 and TFAZ in a molar ratio of 1 : 1 were dispersed in a certain solvent with the assistance of ultrasonic treatment at frequency of 40 kHz for 5 min. A small amount of cocrystal seeds were added to induce the cocrystallization, and the mixture was stirred at 500 rpm under a closed glass vial at 25\(^\circ\)C for 24 h. Finally, the resulting white solids were obtained by filtration, and dried under vacuum to provide cocrystal 1b.

2.2. Structure characterization

A thin piece of dimensions 0.37\(\times\)0.29\(\times\)0.18 mm\(^2\) was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Diffraction data were collected at 296(2) K on a Oxford diffraction Gemini S Ultra diffractometer using Mo-K\(_{\alpha}\) radiation (\(\lambda = 0.071073 \) nm). The structure was solved by direct methods using SHELXS-97 program\textsuperscript{21} and refined against \(F^2\) by full-matrix least-squares using SHELXL-97 program.\textsuperscript{22}
The powder X-ray diffraction patterns were collected with a Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu-Kα radiation (λ = 0.154056 nm). The spectrum was collected by scanning 2θ from 5° to 90°.

The infrared spectra was carried out with a NEXUS B70 spectrometer with KBr pellets by Fourier transform techniques. The spectrums were scanned in the range of 400-4000 cm⁻¹ with resolution ratio of 4 cm⁻¹.

The FEI Quanta 600FEG scanning electron microscope (SEM) was used to study the morphologies of the cocrystals and the coformers at an acceleration voltage of 20 kV. The size distribution of the cocrystal 1b was determined by Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd.)

2.3. Thermal analysis
The differential scanning calorimetry (DSC) tests of the cocrystals and the co-formers were measured with a NETZSCH5 apparatus. The samples (0.6 mg) were placed in aluminum pans and heated at a heating rate of 10 °C min⁻¹ over a range from 30 °C to 400 °C. The TG-DTG experiment of the cocrystal (0.6 mg) was performed with a NETZSCH TG 209F3 instrument operating at a heating rate of 10 °C min⁻¹ in a flow of dry oxygen-free nitrogen at 10 mL min⁻¹ over a range from 30 °C to 500 °C.

2.4. Sensitivity test
The impact sensitivity test was tested according to the Chinese GJB-772A-97 standard method 601.2 with a WL-1 type impact sensitivity instrument. The test conditions were as follows: sample mass, 50 mg; drop weight, 2 kg. The impact sensitivity of each test sample was expressed by the drop height of 50% explosion probability (H₅₀). The friction sensitivity test was determined according to the Chinese GJB-772A-97 standard method 602.1 with a WM-1 type friction sensitivity instrument. The test conditions were as follows: sample mass, 20 mg; relative pressure, 2.45 MPa; and pendulum angle, 66°. The friction sensitivity of each test sample was expressed by explosion probability (Pᵢ).

3. Results and discussion
3.1. Crystal structure
The single crystal X-ray diffraction (SXRD) analysis of cocrystal 1a confirms that it crystallizes in a monoclinic crystal system (space group P2₁) with two CL-20 molecule and two TFAZ molecule in each asymmetric unit. The crystallographic data and intermolecular interactions of 1a are presented in Table 1 and Figure 2, respectively. The cocrystal has high density of 1.932 g cm⁻³ at 296 K, which is somewhat higher than that published previously (1.922 g cm⁻³, 293 K). Interestingly, it is known that the density of γ-CL-20 is 1.92 g cm⁻³, after cocrystallization with a low density conformer TFAZ (1.871 g cm⁻³), the CL-20 molecules also takes on the γ-conformation in this crystal structure, while the crystallographic density of 1a is unexpectedly higher than that of pure γ-CL-20. This effect can be explained by the fact that strong intermolecular interactions exist for increasing of the packing coefficient. As is depicted in Figure 2, 1a exhibits two pairs of intermolecular interactions in terms of the closest intermolecular contacts. One is the intermolecular hydrogen bonds, and the typical hydrogen bond distances and angles are listed in Table 2. It can be found that CL-20 molecule is the donor and TFAZ molecule is the acceptor for all hydrogen bonds. Specifically, H(C) atom of CL-20 molecule forms stronger hydrogen bond with N atom in furazan ring of TFAZ molecule, the bond lengths are 2.484 Å and 2.581 Å, respectively. While another weaker interaction occurs between H(C) atom of CL-20 molecule and O atom of TFAZ molecule, which has a bond length of 3.090 Å. All the above hydrogen bond angle meet the requirement of minimum angle of 110°. The other intermolecular interaction forms between the electron-rich nitro group of CL-20 molecule and the electron-poor furazan ring of TFAZ molecule. The contacts of the N–O···NO₂ type interaction are within the range of 2.842–2.966 Å, which are substantially shorter than the sums of van der Waals radii of the corresponding atoms (3.07 Å). The analogous type of intermolecular interactions also appear in CL-20/BTF cocrystal, therein BTF molecule shares similar fused-furazan ring structure.
with TFAZ molecule. As is noted in Figure 3, the crystal packing of 1a assembles into a zigzag network, and the vacancies between CL-20 molecules are embedded by individual TFAZ molecule, enhancing the crystal stacking density as well as structural and physical stability of explosive.

**Table 1.** Crystal data and structure refinement parameters of cocrystal 1a.

| Cocrystal 1a                                                                 |
|------------------------------------------------------------------------------|
| **Empirical formula** | C₁₂H₇N₁₉O₁₅ | **Formula weight** | 657.37 |
| **Temperature/K** | 296(2) | **Crystal system** | Monoclinic |
| **Space group** | P₂₁ | **Unit cell dimensions/Å, °** | a = 8.288(2), α = 90 |
| | | | b = 11.555(3), β = 91.113(6) |
| | | | c = 11.805(3), γ = 90 |
| **Cell volume/Å³** | 1130.3(5) | **Z** | 2 |
| **ρ_cal/g cm⁻³** | 1.932 | **μ/mm⁻¹** | 0.177 |
| **F(000)** | 664 | **Crystal size/mm** | 0.35 × 0.21 × 0.13 |
| **Goodness-of-fit on F²** | 0.985 | **Final R indexes [I ≥ 2σ]** | $R_1 = 0.0566$, $wR_2 = 0.0787$ |
| | | **R indexes [all data]** | $R_1 = 0.1199$, $wR_2 = 0.0993$ |

**Table 2.** Hydrogen bonds present in cocrystal 1a.

| D−H⋯A | H⋯A/Å | D⋯A/Å | D-H⋯A/° |
|-------|-------|-------|--------|
| C3−H3⋯N14 | 2.484 | 3.356(9) | 148.0 |
| C4−H4⋯N15 | 2.581 | 3.545(8) | 168.6 |
| C3−H3⋯O13 | 3.090 | 4.030(11) | 160.6 |

**Figure 2.** The intermolecular hydrogen bond interactions (a) and N−O⋯NO₂ type interactions (b) between CL-20 and TFAZ molecules found in cocrystal 1a. The lengths of H⋯N, H⋯O, and O⋯N contacts are presented in blue dashed lines.
3.2. Hirshfeld analysis

Hirshfeld surface is an effective tool to reveal and visualize the types and regions of intermolecular interaction in energetic crystals. Here, we use this tool to elucidate the variation of intermolecular interaction after cocrystallization of CL-20 and TFAZ. As shown in Figure 4, the O···O and O···H close contacts account for almost 80% of the total populations in the pure ε-CL-20 crystal, which indicates that these close contacts are the main contribution to the intermolecular interactions. For the pure TFAZ, the populations of the O···O and O···H close contacts decrease significantly, while those of the N···O, N···H, and N···N contacts increase, that may be related to the typical π stacking in TFAZ crystal. When forming a cocrystal, the N···O, O···H, and N···H contacts make up a large proportion of the intermolecular interactions, comprising 28.7%, 17.5%, and 15.1% contributions of the total Hirshfeld surface, respectively. This result shows a good agreement with the analysis of Figure 2. In general, the various form of intermolecular interactions are formed among the CL-20/TFAZ cocrystal during cocrystallization progress, which may provide positive influence on the mechanical properties and safety performance.

Figure 3. The Packing diagram of cocrystal 1a viewed down the a axis. TFAZ molecules are shown in yellow.

Figure 4. 2D fingerprint plots of ε-CL-20, TFAZ, and CL-20/TFAZ cocrystal in crystal stacking as well as close contact populations.
3.3. Preparation and Characterization

The cocrystal 1a was formed initially by growth from isopropyl acetate at 20 °C. However, in individual cases, concomitant growth of colorless spindles of ε-CL-20 were also presented. The cocrystal self-assembly is a process by which two conformers organize spontaneously under near-thermodynamic equilibrium conditions into cocrystal through non-covalent interactions without external guidance, which includes nucleation and crystal growth. Usually the initiation conditions and solvents play an important role in the assembly rate and product quality. To obtain phase-pure cocrystals in a large scale, self-assembly strategy was utilized to prepare cocrystal 1b by optimization with three slightly soluble mediums: hexane, H2O, and H2O/2-propanol. The powder XRD patterns of cocrystal 1a, 1b, and the coformers are presented in Figure 5. As is clearly evident in this figure, the main diffraction angles of 1a localized at 10.61°, 13.12°, 14.98°, 21.39°, 24.18°, and 26.44°, which present significant difference with both the two raw materials. By using hexane as solvent with self-assembly method, the peaks of 12.63°, 13.86°, 25.84°, and 30.35° can be observed clearly in the result product (1b-hexane), it reveals that the crystal phase for ε-CL-20 do not change. In contrast, it is clearly evident in this figure that the PXRD pattern of the self-assembly product from H2O (1b-H2O) is almost the same with that of the cocrystal 1a, validating the formation of pure cocrystalline phase. In addition, when small amount of 2-propanol was added to H2O, the typical diffraction peaks of cocrystal are also visible along with the presence of weak characteristic peaks of ε-CL-20. It may be attributed to the marked difference on the solubility in 2-propanol between CL-20 and TFAZ. That is because the solubility of TFAZ in 2-propanol is far higher than that of CL-20, leading to uncompleted conversion to the cocrystal phase.

We next examined the time of thorough transformation for 1b in H2O, and the PXRD patterns of cocrystal formation process are illustrated in Figure 6. It is showed that the peaks for ε-CL-20 and TFAZ exist simultaneously after 4 h without any characteristic peaks of cocrystal. Next, the peaks of the CL-20/TFAZ cocrystal at 10.61°, 14.91°, 24.21°, and 26.34° appear and grow gradually from reaction time of 12 h to 16 h, accompanied by the reduce of the peaks of two raw materials. Finally, the cocrystallization progress complete after 24 h accompanied by entire disappearance of
characteristic peaks for ε-CL-20. Except for ε polymorphic, no other metastable or thermodynamic phases of CL-20 appear in the assembly process of cocrystal, which is also reflected in CL-20/DNDAP cocrystal reported by our group.\textsuperscript{15} \textbf{1b} was simply isolated by the separation of solid state in high yield (up to 92.3%) and way above that of \textbf{1a} from solvent evaporation (lower than 50%). It can be concluded that CL-20/TFAZ cocrystal can be prepared efficiently by the self-assembly experiment. And more importantly, the one pot procedure for \textbf{1b} in water make the cocrystallization facile, green, and easy scale-up.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{The PXRD patterns of cocrystal \textbf{1b} in H$_2$O at reaction time of 4 h, 12 h, 16 h, and 24 h, respectively.}
\end{figure}

Generally, there are two major types of crystal nucleation: primary crystal nucleation and secondary nucleation.\textsuperscript{27} The cocrystals \textbf{1a} grew in a clear solution without any crystalline material of its own kind, which belong to the primary crystal nucleation. On the other hand, the cocrystals \textbf{1b} generated at presence of cocrystal seeds in a supersaturated suspension, thus they may result from the secondary nucleation. Usually, the cause for inducing secondary nucleation depend on the effect of mechanical forces, the fluid shear, the supersaturation and the addition of crystal seeds.\textsuperscript{28} To get insight into the formation of \textbf{1b} microparticles, a schematic illustration is proposed as presented in Figure 7. Firstly, a small amount of CL-20 and TFAZ dissolve in water as the heterogeneous molecules. Once they contact with cocrystal seeds, the cocrystal nuclei immediately form as a tiny size, and they can also induce secondary nucleation like a catalyst. Combined with Figure 6, after reaching a certain level of concentration of cocrystal nuclei, the secondary nucleation rate is accelerated during the stage from 4 h to 12 h. With an increasing of cocrystal nuclei, the crystal growth can be promoted \textit{via} attachment of particles. Further prolonging the treatment time (24 h), the fully developed cocrystals are completely precipitated from water solution.
The crystal morphologies of raw CL-20, TFAZ, and CL-20/TFAZ cocrystals observed under scanning electron microscope are shown in Figure 8. From Figure 8a and 8b, it is clear that raw CL-20 and TFAZ particles show spindle-shaped and plate-shaped, respectively. Unlike the two coformers, cocrystals 1a present stick shape with a smooth surface (see Figure 8c), and the particle size is about 1 mm with uneven distribution. As shown in Figure 8d, cocrystals 1b are obtained in cubic morphology with a significant decrease of particle size compared with that of 1a. Figure 9 shows the size distribution of 1b by using the laser particle size analyzer. The particle sizes of 1b with cumulative particle size distribution of 10%, 50%, and 90% are assigned to $D_{10}$, $D_{50}$, and $D_{90}$, respectively. Results obtained show that 1b are quite small with a $D_{50}$ value of 8.57 μm, while the $D_{10}$ and $D_{90}$ values of 2.49 μm and 17.32 μm mean a relatively narrow size distribution. Compared with slow evaporation condition, it has been suggested that the rapid and intense agitation with self-assembly approach may increase the nucleation rate, that will lead to a decrease in the cocrystal size. The regular crystal morphologies and small crystal size may contribute to a improved end-use properties of CL-20/TFAZ cocrystals.
3.4. Properties Analysis

Generally, the formation of cocrystal may influence or even make a radical change in their thermal property. Figure 10a shows the DSC curves of CL-20/TFAZ cocrystals as well as two coformers at heating rate of 10 °C/min under atmospheric pressure. As evident from Figure 10a, individual TFAZ begins to melt at 196 °C and completely melts at 198 °C. It is worth noted that no exothermal peak is observed in TFAZ curve, that is because it undergoes evaporation by blowing with nitrogen flow after melting. In the cocrystal 1a, no melting event was observed prior to decomposition, and it exhibits sharp decomposition with onset at 236 °C and maxima at 239.2 °C. One can see that the decomposition onset of CL-20 was marked at 238 °C, thus it may conclude that that decomposition is caused by disintegration of CL-20 molecule, then the reactive gaseous products from CL-20 lead to the decomposition of TFAZ simultaneously. The similar decomposition process was also found in that of CL-20/HMX cocrystals.29 For cocrystal 1b, the peak of decomposition temperature existing is observed at 242.8 °C, which is slightly higher than that of 1a. The narrow temperature range of decomposition process for both two types of cocrystals indicate that they possess high energy release efficiency. The TG–DTG curves of 1a are shown in Figure 10b. It clearly presents that 1a shows a faster weight loss with a steep slope in the TG curve. The decomposition stage occurs in the temperature range of 205–257 °C with a mass loss of 95%. Furthermore, the endothermal peak from the DTG curve is at 226 °C, which is slight lower than the DSC result.

Figure 10. Thermal properties: (a) DSC curves of CL-20, TFAZ, and CL-20/TFAZ cocrystals; (b) TG-DTG curves of cocrystal 1a.

The impact and friction sensitivities of the cocrystal 1b and the coformers were investigated, as shown in Table 3. Remarkably, 1b is found to be relatively insensitive under mechanical stimuli, with
$H_{50}$ value of 42 cm and explosion probability ($P_f$) of 38% towards friction. The sensitivities of 1b are not only considerably lower than that of high explosive CL-20 and HMX, but also significantly lower than that of CL-20/TNT cocrystal.\textsuperscript{30} Furthermore, the sensitivities of physical mixture of CL-20 and TFAZ were also investigated. It was found that the drop height of the mixture is 17 cm, and the explosion probability of friction is 80%. These results suggest that cocrystallization provides an effective method to ameliorate the mechanical sensitivity of CL-20 compared to physical mixture. The following reasons might account for the low mechanical sensitivities of 1b: (1) benefit from the planar structure of TFAZ molecule, the combination of CL-20 and TFAZ molecules can readily lead to interlayer sliding, suggesting the difficult formation of hot spots caused once slide occurs;\textsuperscript{31} (2) the compact and uniform packing may reduce the volume and number of voids in the crystal structure, leading to a reduction in the probability of molecular decomposition under external stimuli.

Benefit from the relative high density of TFAZ (1.87 g cm\textsuperscript{-3}), 1b has a high crystallographic density of up to 1.932 g cm\textsuperscript{-3}, which is much higher than that of most of CL-20/EMs cocrystals such as CL-20/TNT (1.864 g cm\textsuperscript{-3}),\textsuperscript{30} CL-20/BTF (1.918 g cm\textsuperscript{-3}),\textsuperscript{26} and CL-20/DNDAP (1.871 g cm\textsuperscript{-3}),\textsuperscript{15} only slightly lower than that of CL-20/HMX (1.945 g cm\textsuperscript{-3}).\textsuperscript{3} Based on the room-temperature density and calculated heat of formation, the detonation properties including the detonation velocity ($D$) and pressure ($P$) were predicted using EXPLO5 (v 6.02).\textsuperscript{32} From Table 3, it can be found that the predicted detonation velocities and pressures of 1b were 9103 m/s and 37.2 GPa, respectively, which are equally with those of HMX (9110 m/s, 39.3 GPa).\textsuperscript{33} Furthermore, the comparison of density and detonation velocity for nine kinds of CL-20/EMs cocrystals were presented in Figure 11. One can see that except for CL-20/HMX, 1b possesses higher density and detonation velocity values than other seven kinds of CL-20/EMs cocrystals, suggesting that 1b exhibits excellent energetic performance. In general, the high power performance, low mechanical sensitivity, good thermal stability, and high efficiency environment-friendly preparation process suggest 1b a promising high explosive as the substitute for HMX.

Table 3. Detonation properties and sensitivities of the CL-20/TFAZ cocrystal (1b) compared with those of other explosives.

| Explosives                  | $\rho$/g cm\textsuperscript{-3} | $\Delta H_f$/kJ mol\textsuperscript{-1} | $D$/m s\textsuperscript{-1} | $P$/GPa | $H_{50}$/cm | $P_f$/% |
|-----------------------------|---------------------------------|----------------------------------------|------------------------------|---------|-------------|--------|
| $\varepsilon$-CL-20         | 2.04                            | 397.8                                  | 9570                         | 44.3    | 13          | 100    |
| TFAZ                        | 1.87                            | 733.7                                  | 8416                         | 32.9    | 84          | 4      |
| CL-20/TFAZ (1b)             | 1.932                           | 1164.2                                 | 9103                         | 37.2    | 42          | 38     |
| HMX                         | 1.90                            | 87.5                                   | 9110                         | 39.3    | 26          | 84     |
| CL-20/TNT                   | 1.84                            | 940.1                                  | 8426                         | 32.3    | 30          | 58     |

Figure 11. Comparison of the detonation velocity and density of CL-20/EMs cocrystals.
4. Conclusions

In summary, the energetic cocrystal composed of a 1 : 1 molar ratio of CL-20 and TFAZ was successfully prepared via both slow evaporation and self-assembly methods. The SXRD results show that the cocrystal belongs to the monoclinic crystal system based upon intermolecular hydrogen bonds and N–O...NO$_2$ type interactions. Further Hirshfeld surface analysis shows that the N...O, O...H, and N...H contacts make up a large proportion of the intermolecular interactions. The cocrystals $1b$ were formed in pure water with the yield up to 92.3%, and both $1a$ and $1b$ were fully characterized by P-XRD analysis. $1b$ are cubic-like in shape with particle size ranging from 2.49 $\mu$m to 17.32 $\mu$m. These cocrystals exhibit high energy release efficiency and unique exothermic peak at 239.2 °C and 242.8 °C, respectively. Further investigations showed that $1b$ possesses higher density, equal detonation velocity, and considerably lower mechanical sensitivity than that of HMX. This work not only provides a high performance energetic cocrystal with reduced sensitivity, but also opens up a new advance in development of environment-friendly preparation of energetic cocrystals. We believe that this self-assembly method may play an important role in industrial production of energetic cocrystals on a large scale.

References

[1] Piercey D G, Chavez D E, Scott B L, Imler G H and Parrish D A 2016 Angew. Chem. Int. Ed. 55 15315
[2] Badgujar D M, Talawar M B, Asthana S N and Mahulikar P P 2008 J. Hazard. Mater. 151 289
[3] Simpson R L, Urtiew P A, Ornellas D L, Moody G L, Scribner K J and Hoffman D M 1997 Propellants, Explos., Pyrotech. 22 249
[4] Zhang J and Shreeve J M 2016 CrystEngComm 18 6124
[5] Kent R V, Wiscons R A, Sharon P, Grinstein D, Frimer A A and Matzger A J 2018 Cryst. Growth Des. 18 219
[6] Zhang C, Xue X, Cao Y, Zhou J, Zhang A, Li H, Zhou Y, Xu R and Gao T 2014 CrystEngComm 16 5905
[7] Bolton O, Simke L R, Pagoria P F and Matzger A J 2012 Cryst. Growth Des. 12 4311
[8] Bolton O and Matzger A J 2011 Angew. Chem. Int. Ed. 50 8960
[9] Anderson S R, Dubé P, Krawiec M, Salan J S, Ende D J and Samuels P 2016 Propellants, Explos., Pyrotech. 41 783
[10] Zhang X, Chen S, Wu Y, Jin S, Wang X, Wang Y, Shang F, Chen K, Du J and Shu Q 2018 Chem. Comm. 54 13268
[11] Yang Z, Wang H, Ma Y, Huang Q, Zhang J, Nie F, Zhang J and Li H 2018 Cryst. Growth Des. 18 6399
[12] Gao B, Wang D, Zhang J, Hu Y, Shen J, Wang J, Huang B, Qiao Z, Huang H, Nie F and Yang G 2014 J. Mater. Chem. A 2 19969
[13] Doblás D, Rosenthal M, Burghammer M, Chernyshov D, Spitzer D and Ivanov D A 2016 Cryst. Growth Des. 16 432
[14] Qiu H, Patel R B, Damavarapu R S and Stepanov V 2015 CrystEngComm 17 4080
[15] Liu N, Duan B, Lu X, Mo H, Xu M, Zhang Q and Wang B 2018 CrystEngComm 20 2060
[16] Duan B, Shu Y, Liu N, Wang B, Lu X and Lu Y 2018 CrystEngComm 20 5790
[17] Duan B, Shu Y, Liu N, Lu Y, Wang B, Lu X and Zhang J 2018 RSC Adv. 8 34690
[18] Liu N, Duan B, Lu X, Mo H, Bi F, Wang B, Zhang J and Yan Q L 2019 Propellants, Explos., Pyrotech. 44 1242
[19] Jia S, Zhang H, Zhou C, Lai W, Li X and Wang B 2015 Chin. J. Org. Chem. 35 851
[20] Aldoshin S M, Aliev Z G, Goncharov T K, Miilyokin Yu M, Shishov N I, Astratyev A A, Dashko D V, Vasilyeva A A and Stepanov A I 2014 J. Struct. Chem. 55 327
[21] Sheldrick G M 1997 SHELXS-97, Program for solution of crystal structures (University of Gottingen)
[22] Sheldrick G M 1997 *SHELXS-97, Program for refinement of crystal structures* (University of Gottingen)
[23] National Military Standard of China 1997 *Experimental Methods of Sensitivity and Safety GJB/772A-97* (in Chinese)
[24] Ghosh M, Venkatesan V, Mandave S, Banerjee S, Sikder N, Sikder A K and Bhattacharya B 2014 *Cryst. Growth Des.* **14** 5053
[25] Steiner T 2002 *Angew. Chem., Int. Ed.* **41** 48
[26] Yang Z, Li H, Zhou X, Zhang C, Huang H, Li J and Nie F 2012 *Cryst. Growth Des.* **12** 5155
[27] Briuglia M L, Sefcik J and ter Horst J H 2019 *Cryst. Growth Des.* **19** 421
[28] Zhang D, Wang X, Ulrich J, Tang W, Xu S, Li Z, Rohani S and Gong J 2019 *Cryst. Growth Des.* **19** 3070
[29] Ghosh M, Sikder A K, Banerjee S and Gonnade R G 2018 *Cryst. Growth Des.* **18** 3781
[30] Yang Z, Li H, Huang H, Zhou X, Li J and Nie F 2013 *Propellants, Explos., Pyrotech.* **38** 495
[31] Ma Y, Zhang A, Zhang C, Jiang D, Zhu Y and Zhang C 2014 *Cryst. Growth Des.* **14** 4703
[32] Sučeska M 2013 *EXPLO5 Version 6.02* (Zagreb: Brodarski Institute)
[33] Tian D Y, Zhao F Q and Liu J H 2011 *Handbook of Energetic Materials and the Related Compounds* (Beijing: National Defense Industry Press)