Supporting Information

Hydrogen-Bonded Ammonium Dinitramide/Dibenzo-[18]-Crown-6 Cocrystal with Low Hygroscopicity and Reduced Sensitivity

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Characterizations

Characterization was conducted using a Bruker Tensor 27 FTIR spectrometer, and a compressed disc method was exploited, in which the sample was ground with potassium bromide and pressed into a pellet. The measurements were performed using 32 scans at a resolution of 1 cm^{-1}, covering a wavenumber range of 400-4000 cm^{-1}. This approach delivered accurate information for identifying molecular vibrations and functional groups. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECZ600R NMR spectrometer (600 MHz) to determine the molecular structure. The samples were dissolved in either $CDCl_3$ or DMSO-d6. Tetramethylsilane (TMS) served as the external standard for calibrating the chemical shifts. Chemical shifts were indicated in parts per million (ppm). The hygroscopicity test was conducted using the Suncheer temperature and humidity chamber (FIRSTEK BTH80/-20) and a Mettler Toledo analytical balance (LE204E). The weight gain method was utilized to assess the hygroscopic properties of these materials. Samples of ADN and the cocrystal, both in a dry state, were contained in individual glass bottles, and their starting weights were recorded. The samples were subsequently positioned in the temperature and humidity chamber maintained at 30 ℃ and 60% relative humidity for a duration of 12 hours. Samples were removed from the chamber every hour, and their weights were recorded to calculate the increase in weight gain. The hygroscopicity rate (H_y) was determined by the formula provided below:

$$H_y = \frac{(M_x - M_i)}{M_i} \times 100\ \%$$

where M_i indicates the initial weight of the sample, while M_x refers to the sample weight after absorbing moisture at different time x. Differential scanning calorimetry (DSC) was carried out using a TA Instruments DSC 2920 device. The procedure involved placing a sample weighing 3-5 mg into an aluminum pan and sealing it using a hydraulic press tool. The measurements were performed within a temperature range from 40 to 500 °C in a nitrogen environment. The heating scan rate was 10 ℃/min. The powder X-ray diffraction (PXRD) measurements were obtained by a Bruker D8 Advance diffractometer, employing Cu-Kα radiation (λ = 1.54439 Å). Diffraction patterns for both

the newly formed cocrystal and the raw materials were recorded. The instrument operated at 30 kV and 10 mA, collecting data for the samples with a scan rate of 1 second per step within the range of 5-50 (step size: 0.1). The structure of the cocrystal was identified using single-crystal X-ray diffraction (SXRD) with IμS Diamond II Cu radiation (λ=1.54178 Å). Data collection was performed using Bruker AXS D8 VENTURE diffractometer at a temperature of 100 K, covering the angular range from 3.74 to 70.07 degree. The arrangement and packing of the unit cell were visualized through the CCDC Mercury software. The test for impact sensitivity (IS) was conducted by subjecting 30 mg samples to a 2 kg drop hammer (BAM fall hammer). The results were expressed as E50%, indicating the impact of energy corresponding to a 50% probability of detonation.

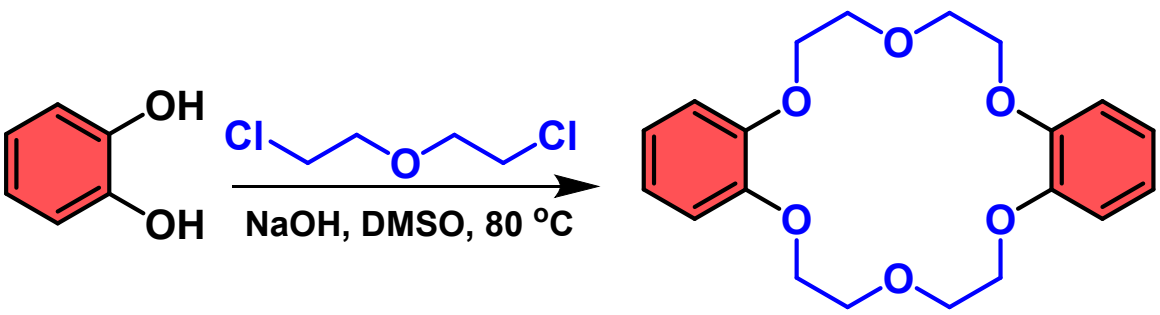

Figure S1. Synthesis of DB18C6.

Table S1. Crystallographic information regarding the ADN/DB18C6 cocrystal.

Structure parameter	ADN/DB18C6
Formula	$C_{60}H_{80}N_8O_{26}$
Temperature/K	100
Stoichiometry	2:3
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.9630(5)
b (Å)	12.6139(4)
c (Å)	19.5836(7)
α (°)	90
β (°)	102.8104(13)
γ (°)	90
Volume ($Å^3$)	3122.49(19)
Z	2
ρ calc ($g \cdot cm^{-3}$)	1.414
F (000)	1408
Crystal size (mm^3)	0.150 x 0.150 x 0.100
Independent reflections	5875
GOF	2.053
R1, wR2 ($I \geqq 2\sigma(I)$)	0.0560,0.2323
R1, wR2 (all data)	0.0577,0.2354

Table S2. Hydrogen Bond lengths and angles for the ADN/DB18C6 cocrystal within the NH_4^+ cation.

N1–H1A···O12 hydrogen bond: H1A···O12 = 2.035 Å, N1···O12 = 2.835 Å, N1–H1A···O12 = 153.3°
N1–H1B···O3 hydrogen bond: H1B···O3 = 2.008 Å, N1···O3 = 2.862 Å, N1–H1B···O3 = 176.9°
N1–H1C···O5 hydrogen bond: H1C···O5 = 1.956 Å, N1···O5 = 2.815 Å, N1–H1C···O5 = 166.9°
N1–H1D···O1 hydrogen bond: H1D···O1 = 2.040 Å, N1···O1 = 2.912 Å, N1–H1D···O1 = 173.7°

Table S3. Specific impulse prediction of different oxidizers applied in solid propellant formulation.

oxidizer	AP	ADN	ADN/DB18C6 cocrystal
Isp (s)	243.1	246.4	199.4

*The solid propellant formulations consisted of HTPB (12 wt%), aluminum powder (25 wt%), oxidizer (60 wt%), and additives (3 wt%). The theoretical propulsion performance was calculated using the NASA CEA (Chemical Equilibrium with Applications) code.