

Supporting Information

Hydrogen Peroxide Solvates of 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

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ange_201607130_sm_miscellaneous_information.pdf

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SI 1. Experimental

Caution: Although no unplanned detonations were encountered during this work, CL-20 is a dangerous high explosives and hydrogen peroxide is a strong oxidizing agent. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, or impact. Be aware that the potential for severe injury exists if these materials are handled improperly.

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) was used as received from Picantiny Arsenal. The concentrated 98% hydrogen peroxide (HP) was used as received from PeroxyChem LLC.

Crystallization

Both polymorphic solvates of CL-20 (**1** and **2**) were initially obtained from 1:1 acetonitrile/HP solutions, with a small amount (~5 mg) of CL-20 dissolved, by slow evaporation and then conditions for their pure growth was determined. Similarly, the hydrated form of α -CL-20 was obtained by slow evaporation by dissolving a small amount (~5 mg) of CL-20 in a 1:1 acetonitrile/DI H₂O solution. The orthorhombic solvate could be scaled up easily through the slow addition of HP to the solution of CL-20. The monoclinic solvate could be scaled up conveniently with the use of solvent mediated transformation in a slurry of the pure components at room temperature, see below.

2:1 CL-20/HP (1) monoclinic

A 4 mL glass vial was loaded with 30 mg of ϵ -CL-20 (0.0685 mmol) which was dissolved in 300 μ L of dry acetonitrile. To this was added 300 μ L of concentrated H₂O₂ at which point the formation of thin plates of **1** was observed by optical microscopy. The vial was sealed/stirred gently for 15 minutes, before the crystal were collected. This solid was determined to be the 2:1 CL-20/HP orthorhombic solvate by both Raman spectroscopy and powder X-ray diffraction.

2:1 CL-20/HP (2) monoclinic

A 4 mL glass vial was loaded with 30 mg of ϵ -CL-20 (0.0685 mmol) which was dissolved in 200 μ L of dry acetonitrile. To this was added 500 μ L of concentrated H₂O₂ at which point a mixture

of orthorhombic and monoclinic solvates was obtained. The vial was sealed/stirred gently for 4 days, during which time the orthorhombic CL-20/HP crystals had disappeared and only the monoclinic CL-20/HP remained by optical microscopy. This solid was determined to be the 2:1 CL-20/HP monoclinic solvate by both Raman spectroscopy and powder X-ray diffraction.

Raman Spectroscopy

Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope, 633 nm laser, 1800 lines/mm grating, 50 μm slit and a RenCam CCD detector. Spectra were collected in extended scan mode with a range of 100-4000 cm^{-1} and then analyzed using the WiRE 3.4 software package (Renishaw). Calibration was performed using a silicon standard.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer using Cu-K α radiation ($\lambda = 1.54187 \text{ \AA}$) and operating at 40 kV and 40 mA. Samples were prepared by finely grinding and packing into the depression of a glass slide. The powder patterns were collected by scanning 2θ from 5° to 50° with a step size of 0.02° and a step speed of 0.5 seconds. The data was processed using Jade 8 XRD Pattern Processing, Identification & Quantification analysis software (Materials Data, Inc.).¹ The powder patterns were all compared to their respective simulated powder patterns from the single crystal X-ray diffraction structures and were found to be in significant agreement with the predicted patterns.

Single Crystal Structure Determination

Single crystal X-ray diffraction data for **1**, **2** and α -CL-20 were collected using a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187 \text{ \AA}$) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. The data was processed with CrystalClear 2.0 (Rigaku)² and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 2008/4)³ software package using direct methods. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized

positions. Funding for single crystal X-ray analysis was from NSF Grant CHE-0840456 for the Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer.

CCDC 1495519, 1495520 and 1495521 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table S1. Crystallographic Data for α -CL20 and CL-20 Solvates (Collected at 85 K)

Material	α -CL-20	1	2
Stoichiometry	4:1	2:1	2:1
Morphology	Plate	Rhombic	Polyhedron
Space Group	Pbca	Pbca	C2/c
a (Å)	9.4765(2)	9.4751(2)	28.4497(7)
b (Å)	13.1394(2)	13.1540(10)	8.9596(2)
c (Å)	23.3795(16)	23.4266(4)	12.7807(9)
α (°)	90	90	90
β (°)	90	90	113.397(8)
γ (°)	90	90	90
V_{Ovolume} (Å ³)	2911.11	2919.79	2989.9
Z	8	8	8
ρ_{calc} (g/cm ³)	2.020	2.071	2.041
Data/Parameter	2669/287	2648/324	2696/312
R_1/wR_2	3.46/9.38	3.28/8.82	4.10/9.49
GOF	1.008	1.058	1.134

Differential Scanning Calorimetry (DSC)

Thermograms for each samples were recorded on a TA Instruments Q20 DSC equipped with a RCS90 chiller. All experiments were run in Tzero™ hermetic aluminum DSC pans under a nitrogen purge with a heating rate of 10 °C/min, while covering the temperature range of 40 °C to 300 °C. The instrument was calibrated using an indium standard. Thermograms were analyzed using TA Universal Analysis 2000, V 4.5A.

Thermogravimetric Analysis (TGA)

Thermograms for each samples were recorded on a TA Instruments Q50 TGA. All experiments were run in platinum TGA sample pans with a stainless steel mesh cover under a nitrogen purge of 50 mL/min with a heating rate of 10 °C/min, while covering the temperature range of 35 °C to 450 °C. The instrument was calibrated using the Curie points of alumel and nickel standards. Thermograms were analyzed using TA Universal Analysis 2000, V 4.5A.

Drop Weight Impact Sensitivity Analysis

For the analysis of the sensitivity to impact, approximately 2 mg ($\pm 10\%$) of material for each sample is contained within nonhermetic DSC pans and then struck by a freefalling 5 lb drop weight. A reproducible Dh_{50} , height of the 50% probability of detonation, is obtained by utilizing the Bruceton Analysis (up-and-down method) with varying drop heights. For reference the Dh_{50} of ϵ -CL-20 and β -HMX are 29 and 55 cm, respectively.

SI 2. Powder X-ray Diffraction of CL-20 Solvates

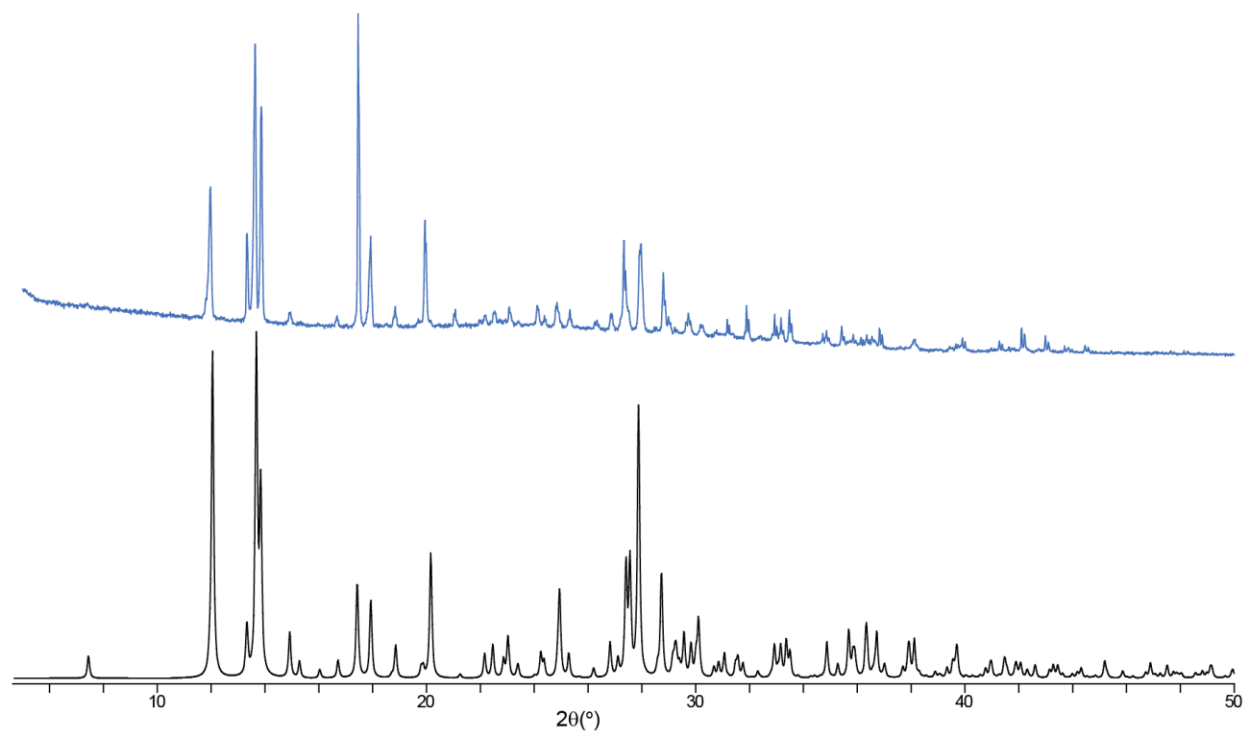


Figure S1. Powder patterns of **1** and the simulated structure of α -CL-20 from the CIF (from top to bottom).

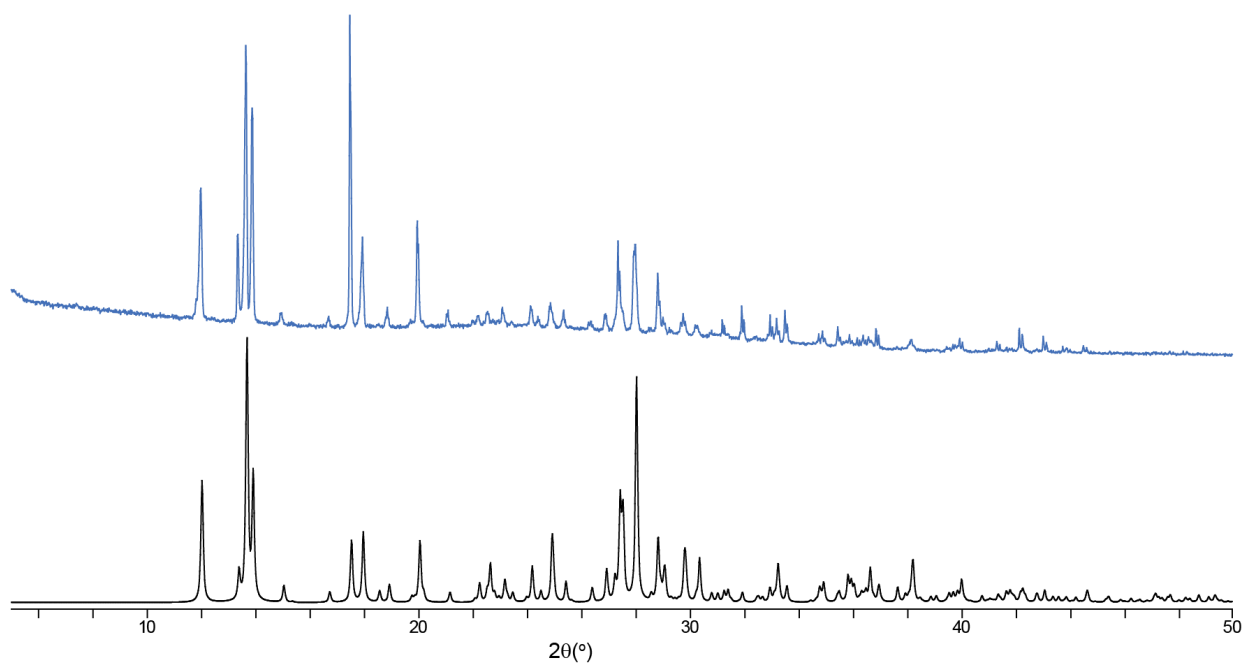


Figure S2. Powder patterns of **1** and the simulated structure of **1** from the CIF (from top to bottom).

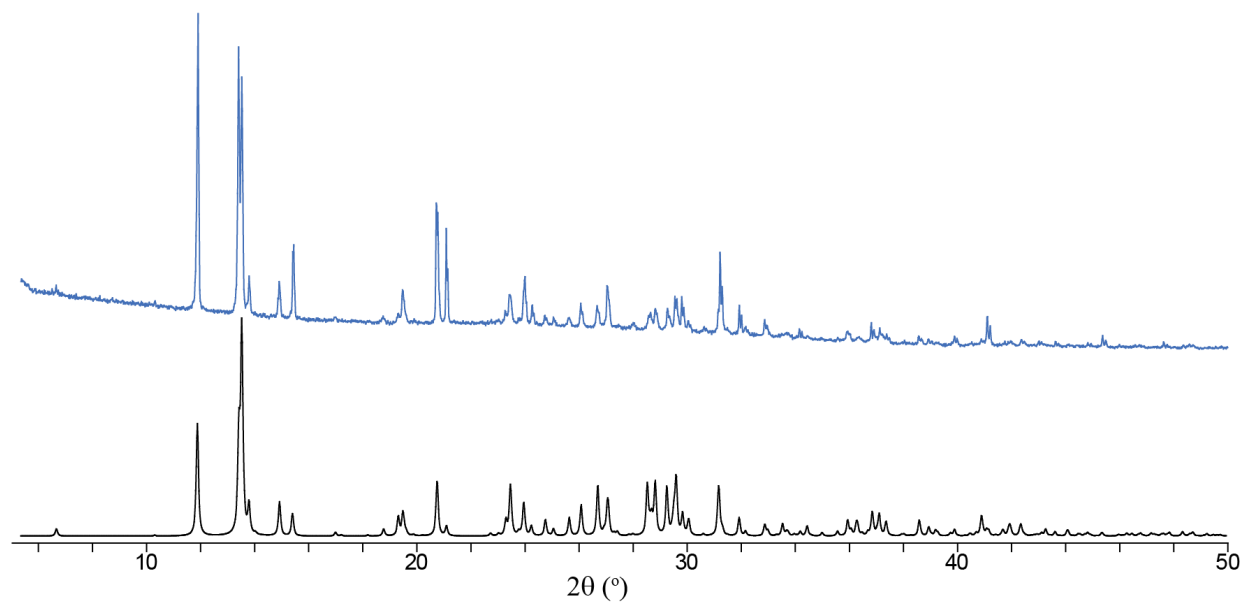


Figure S3. Powder patterns of **2** and the simulated structure of **2** from the CIF (from top to bottom).

SI 3. Raman Spectroscopy of CL-20 Solvates

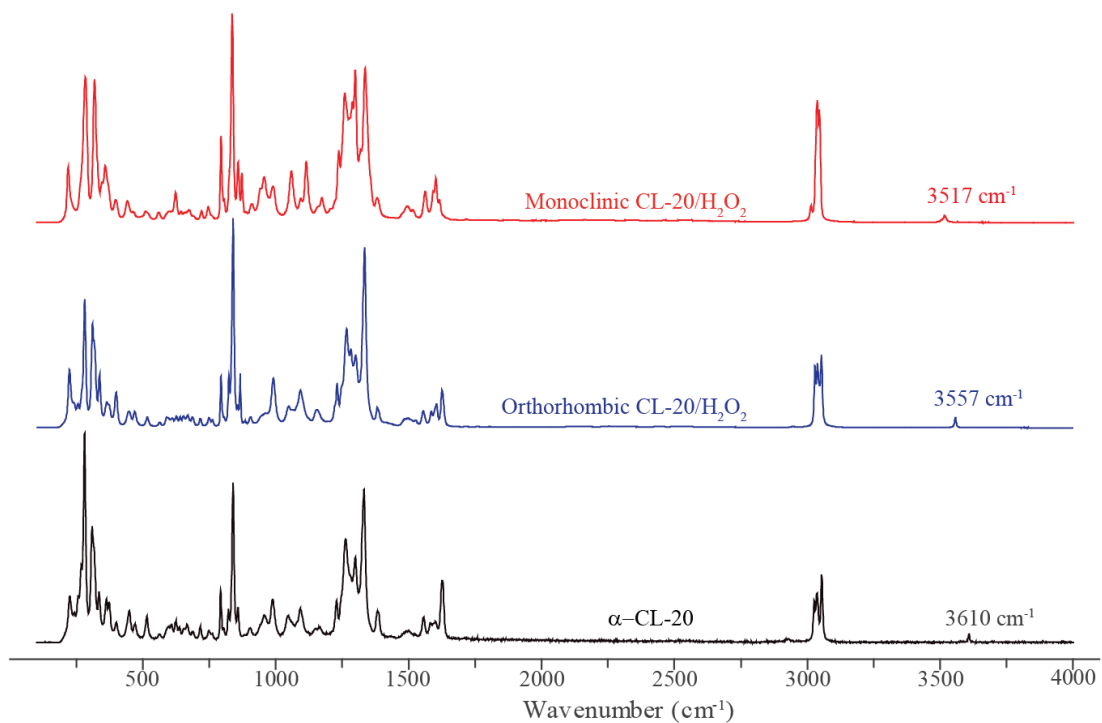


Figure S4. Full range (100-4000 cm⁻¹) Raman spectra of α-CL-20, **1** and **2** (from bottom to top).

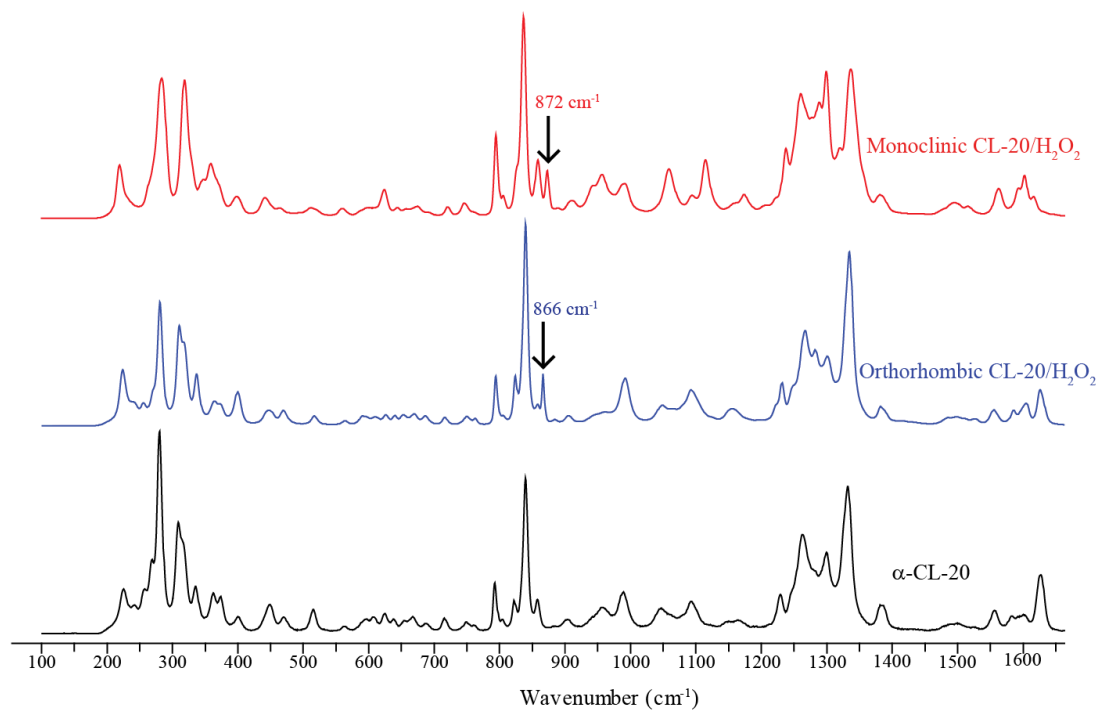


Figure S5. Zoomed in (100-1650 cm⁻¹) Raman spectra of α-CL-20, **1** and **2** (from bottom to top). Pure HP O-O peak is at 879 cm⁻¹.

SI 4. ORTEP Diagrams of CL-20 Solvates

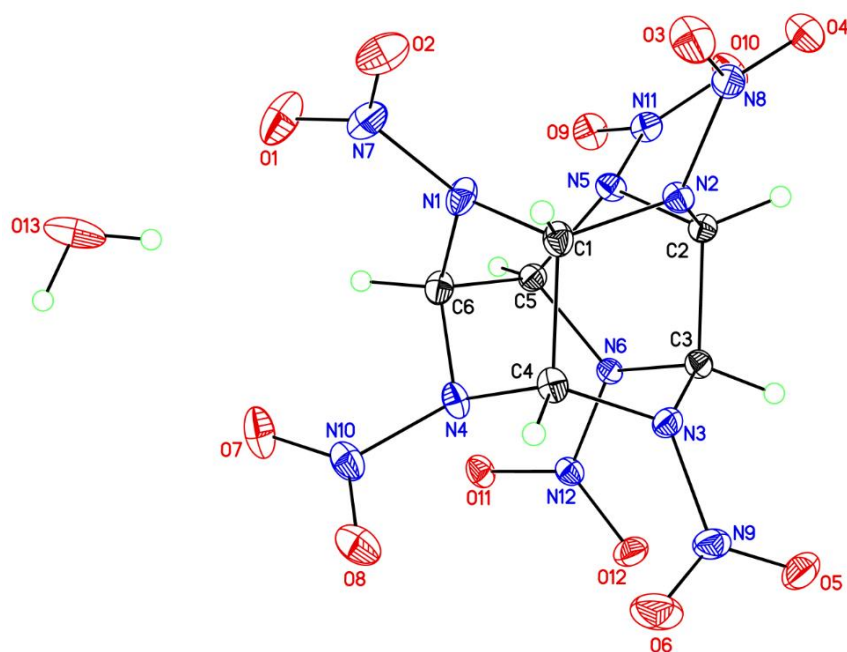


Figure S6. ORTEP diagram for α -CL-20 collected at 85 K with thermal ellipsoids of 50% probability.

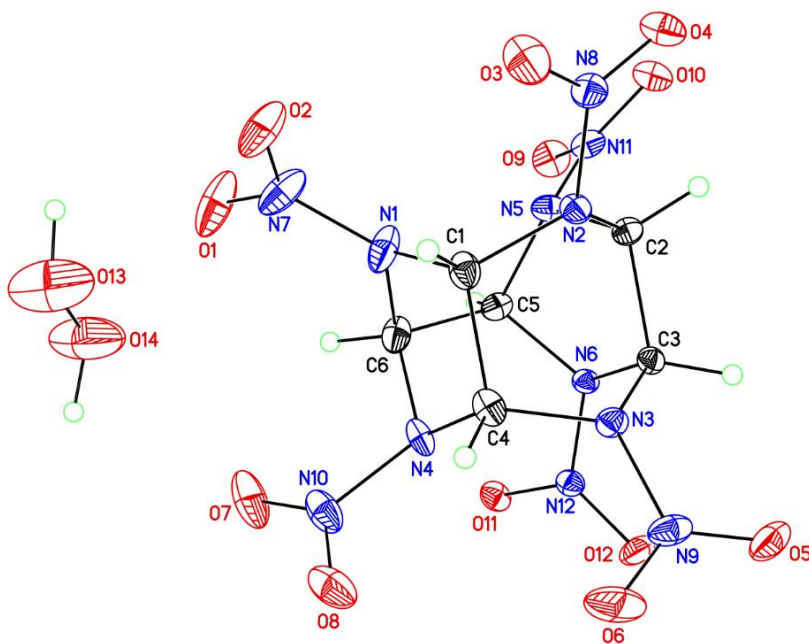


Figure S7. ORTEP diagram for **1**, orthorhombic, collected at 85 K with thermal ellipsoids of 50% probability.

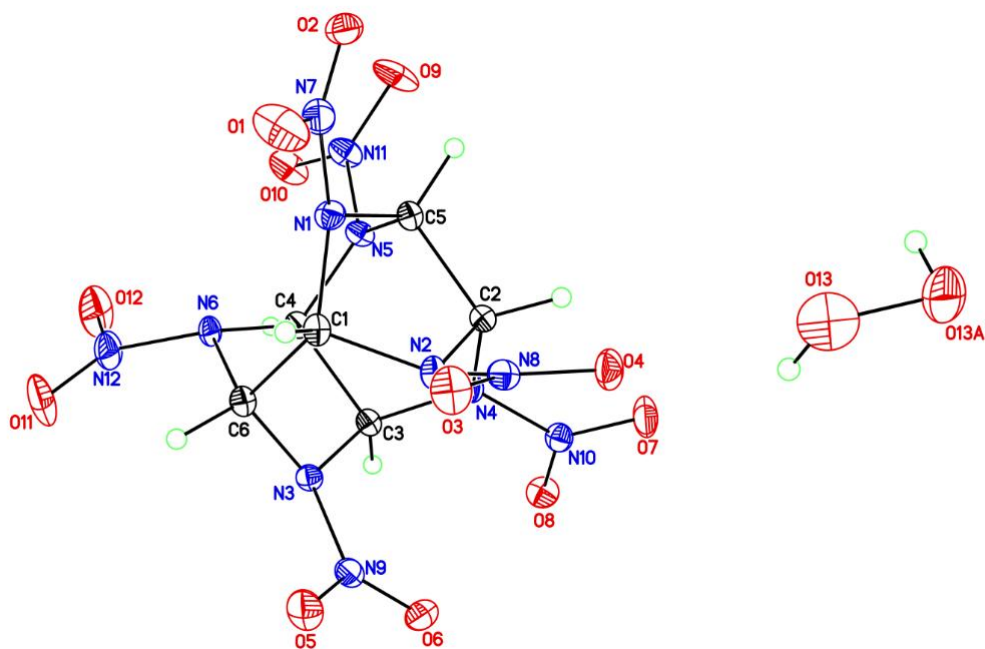


Figure S8. ORTEP diagram for **2**, monoclinic, collected at 85 K with thermal ellipsoids of 50% probability.

SI 5. Differential Scanning Calorimetry of CL-20 Solvates

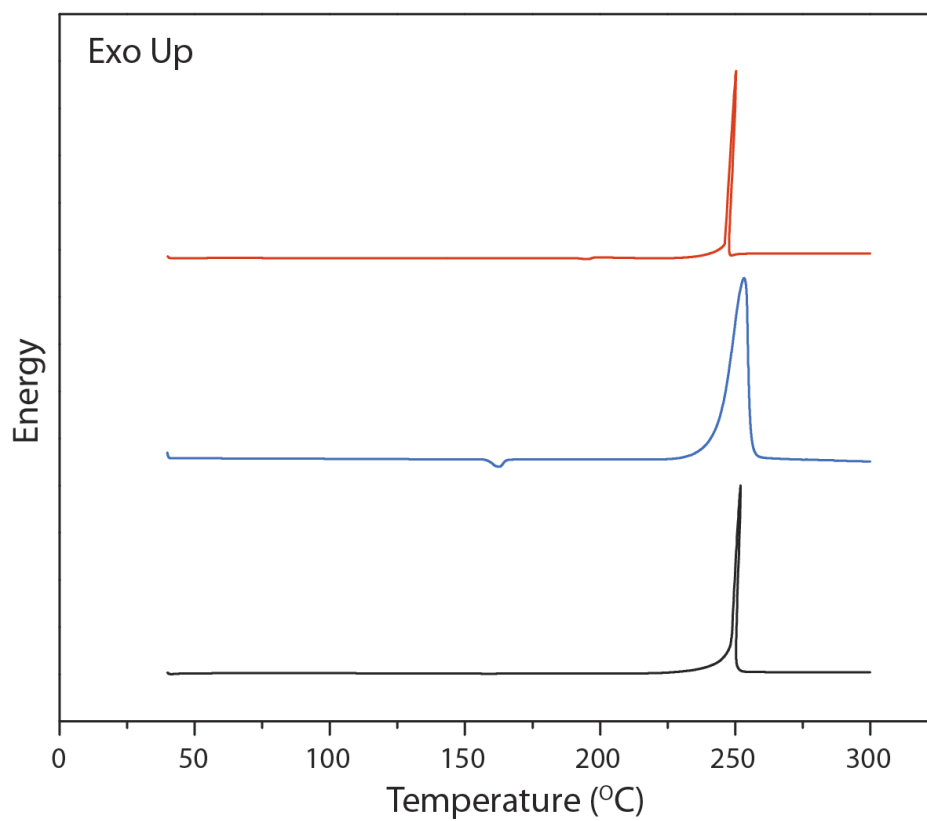


Figure S9. Typical DSC traces of α -CL20, **1** and **2** (from bottom to top).

SI 6. Thermogravimetric Analysis of CL-20 Solvates

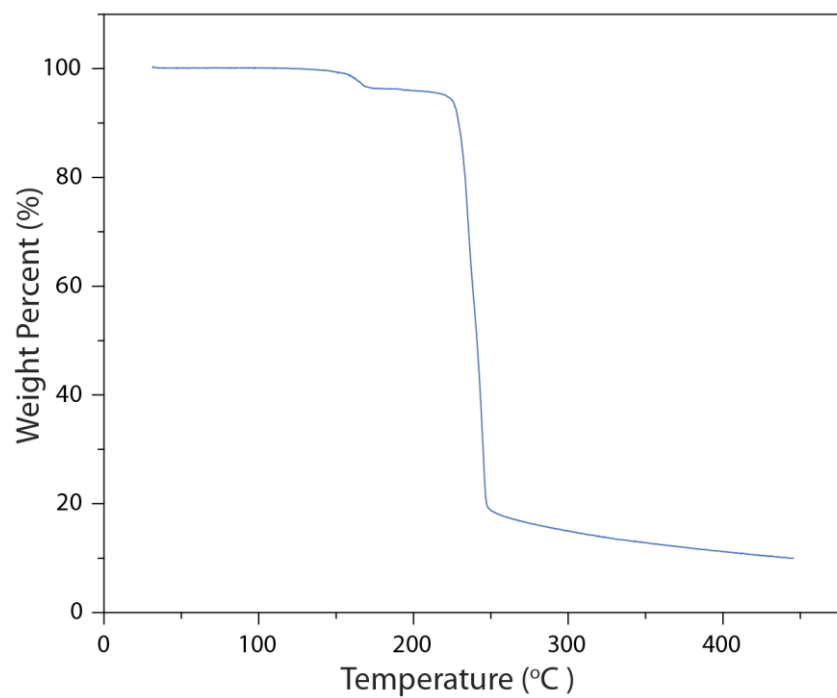


Figure S10. Typical TGA traces of **1**.

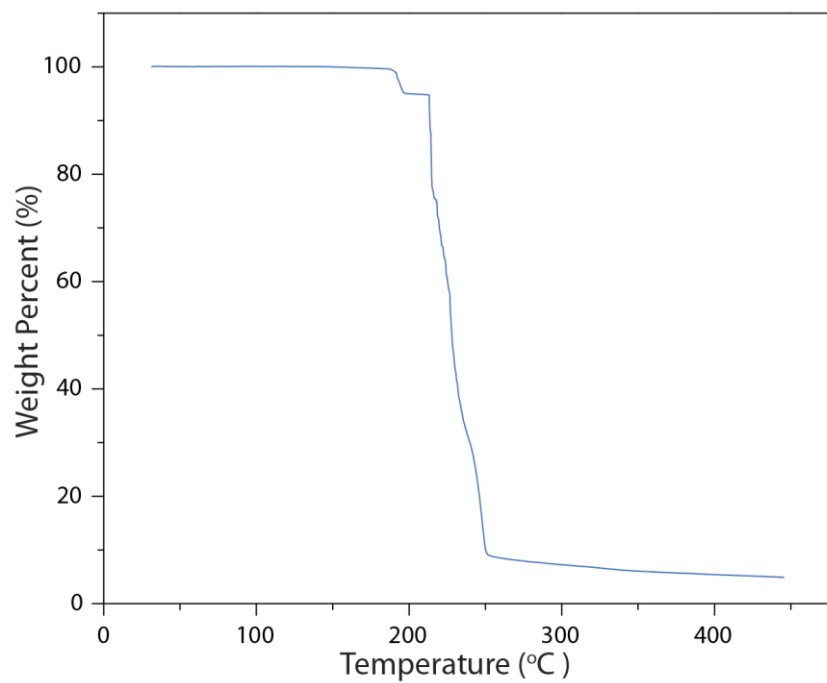


Figure S11. Typical TGA traces of **2**.

SI 7. Morphology of CL-20 Solvates

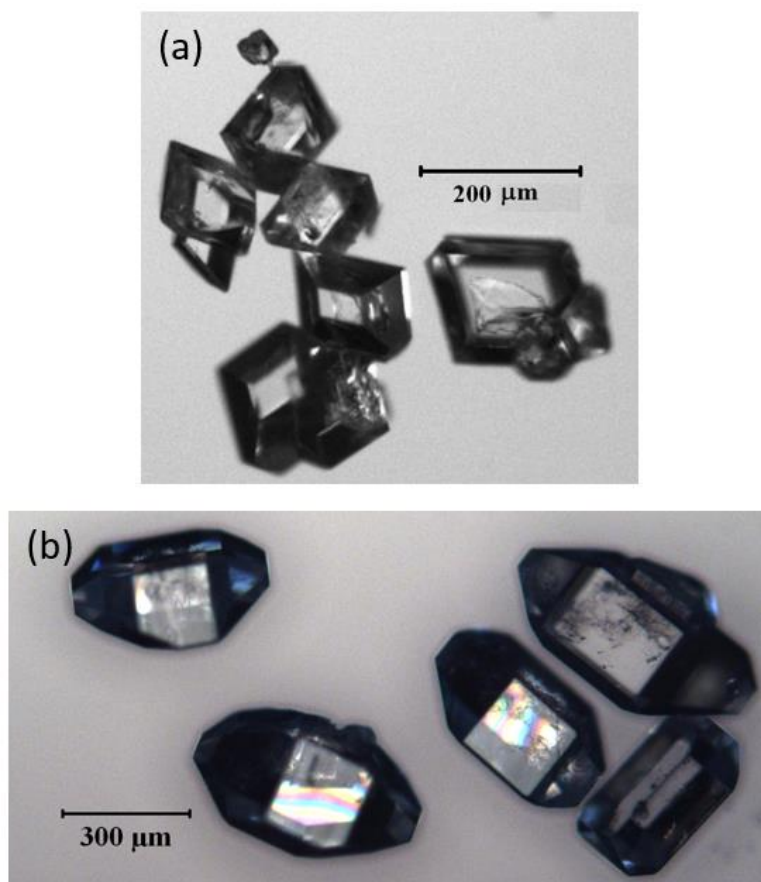


Figure S7. Typical habit morphology of the two polymorphs of the 2:1 CL-20/HP solvates (**1** and **2**): (a) orthorhombic; (b) monoclinic.

SI 8. References

- (1) Jade Plus 8.2 ed.; Materials Data, Inc. 1995-2007.
- (2) CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
- (3) Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.