Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Information

Bulk Growth and Physical Properties of Diguanidinium Phosphate Monohydrate (G2HP) as a Multi-functional Crystal

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Table 1S Crystal data and structure refinement for G2HP

Fig. 1S The molecular structures and orientations of the models for calculation: (Ⅰ) G2HP molecule, (Ⅱ) LAP molecule, (Ⅲ) Guanidyl cation 1, (Ⅳ) Guanidyl cation 2 and (Ⅴ) PO_4 tetrahedron

Fig. 2S Two typical factual growth morphologies (a); theoretical morphology predicted by the BFDH model (b).

Table 2S Comparison of dipole moment (in D), linear polarizability (in 10^{-24} esu) and first hyperpolarizability (in 10^{-30} esu) values for G2HP and LAP

Table 1S Crystal data and structure refinement for G2HP

Empirical formula	$C_2H_{15}N_6O_5P$
Radiation λ (Mo Kα) (Å)	0.71073
Molecular weight	234.17
Temperature (K)	296(2)
Description	Prism
Color	Colorless
Crystal size (mm)	0.16 × 0.13× 0.12
Crystal system	Tetragonal
Crystal group	$P\text{-}42_1c$
a(Å)	16.8420(2)
c(Å)	7.2490(2)
V(Å^3)	2056.20(7)
Z	8
$D_{cal.}$ (mg·m^{-3})	1.513
Absorption coefficient (mm^{-1})	0.281
Absorption correction T_{min} and T_{max}	0.9671 and 0.9564
F (0 0 0)	992
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0313, wR_2 =0.0690
R indices (all data)	R_1 = 0.0423, wR_2 = 0.0752
Data/restraints/parameters	2314 / 0 / 188
Goodness-of-fit on F^2	1.024
Largest diff. peak and hole/Å^{-3}	0.160 and -0.209

Single-Crystal X-ray Diffraction.

A colorless and transparent crystal was selected to the desired dimensions of about 0.16 × 0.13 × 0.12 mm^3, which was then mounted on a glass fiber by glue to perform the data collection using a Bruker Smart Apex-II CCD diffractometer with Mo K*α* radiation (λ = 0.71073 Å) at 296(2) K. Preliminary lattice parameters and orientation matrices were indexed from three sets of frames. Data integration and cell refinement were carried out by the INTEGRATE program of the APEX2 software,[1] and multiscan absorption corrections were done using the SCALE program.[1] The structure was solved in space group $P\text{-}42_1c$ (No. 114) by

direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX.[2] All non-hydrogen atoms were refined with anisotropic thermal parameters, and the refinements converged for $I > 2\sigma(I)$. All calculations were performed using the SHELXTL crystallographic software package. Structures were also checked for possible missing symmetry with PLATON.[3] Crystallographic data and structural refinements are summarized in Table 1S. More details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information.

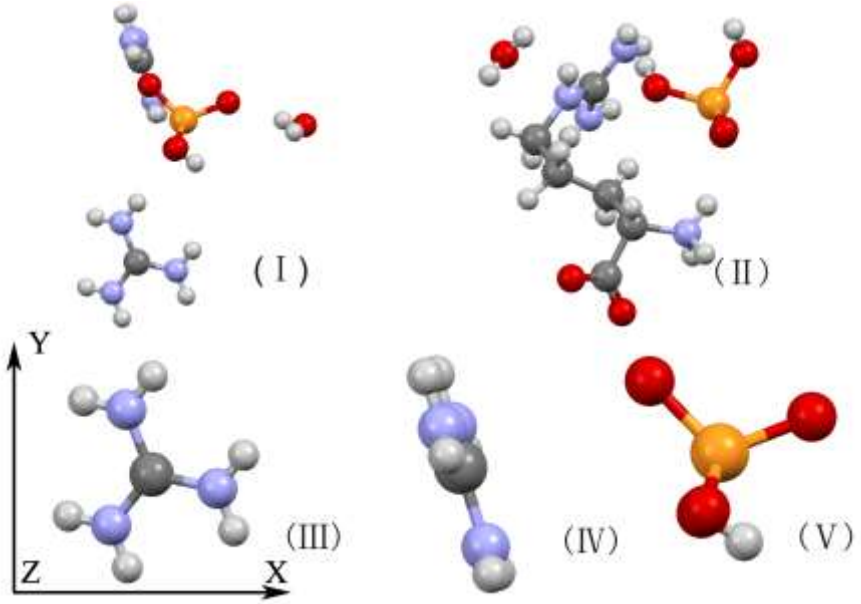

Fig. 1S The molecular structures and orientations of the models for calculation: (Ⅰ) G2HP molecule, (Ⅱ) LAP molecule, (Ⅲ) Guanidyl cation 1, (Ⅳ) Guanidyl cation 2 and (Ⅴ) PO_4 tetrahedron

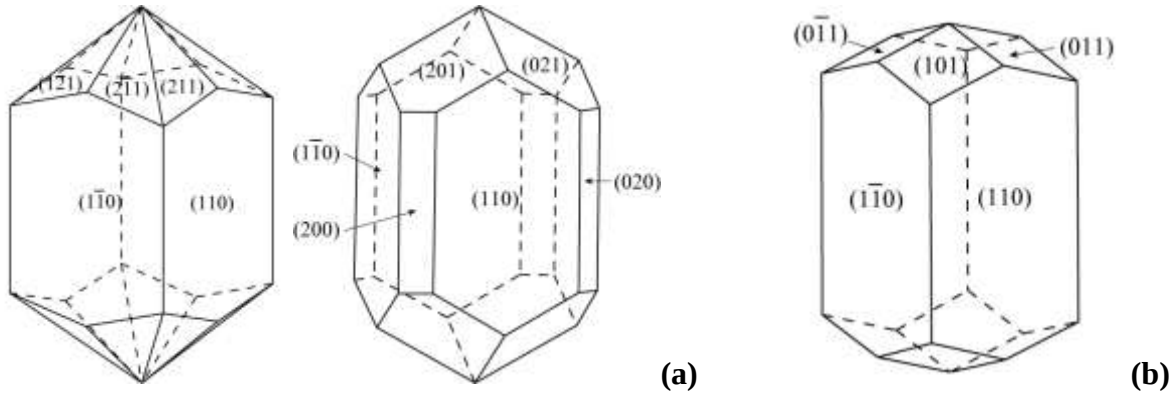

Fig. 2S Two typical factual growth morphologies (a); theoretical morphology predicted by the BFDH model (b).

Crystal Growth Morphology.

The morphology of a crystal is a reflection of its structure which was mainly determined by the relative growth rates of various facets. The growth morphology of G2HP crystal was also indexed on the diffractometer combined with measuring the interfacial angles in the habit (Fig. 1S). The {110}, {020}, {021}, and {211} facets were formed during the crystal growth. The theoretical morphology of G2HP crystal was also predicted by the Bravais-Friedel-Donnay-Harker (BFDH)[4] model using the Mercury program,[5] which is presented in Fig. 1S (b). It is worth noting that the two morphologies (Fig. 1S (a) and (b)) are largely the same but with a little difference which may be attributable to growth conditions such as seed orientation, solvent supersaturation, pH value, temperature, impurities, hydrodynamics and cooling rate.

Table 2S Comparison of dipole moment (in D), linear polarizability (in 10^{-24} esu) and first hyperpolarizability (in 10^{-30} esu) values for G2HP and LAP

	Guanidyl cation 1	Guanidyl cation 2	PO_4 tetrahedron	G2HP	LAP
μ_x	-0.001	0.001	0.402	3.645	-2.205
μ_y	0.010	0.005	0.728	-2.290	-6.619
μ_z	0.005	0.002	0.555	-0.401	-3.876
u_g	**0.011**	**0.006**	**1.000**	**4.323**	**7.981**
α_{xx}	3.093	4.322	5.457	24.254	13.684
α_{xy}	0.445	0.105	0.073	0.861	0.165
α_{yy}	4.335	4.401	5.238	17.521	15.129
α_{xz}	0.114	-0.455	0.079	0.901	1.357
α_{yz}	-0.024	0.284	-0.052	0.472	1.856
α_{zz}	4.474	3.158	5.401	16.486	14.365
α_{tot}	**3.967**	**3.960**	**5.365**	**19.420**	**14.392**
β_{xxx}	0.011	0.384	-0.053	-0.413	3.187
β_{xxy}	0.041	0.189	0.009	0.381	1.251
β_{xyy}	0.131	-0.371	0.040	-0.659	0.679
β_{yyy}	0.414	-0.261	-0.078	0.861	3.364
β_{zxx}	-0.024	-0.093	-0.048	-0.166	1.170
β_{xyz}	-0.030	-0.146	-0.038	0.066	0.268
β_{zyy}	0.013	0.068	0.105	0.038	1.106
β_{xzz}	-0.153	0.002	-0.039	-0.075	1.040
β_{yzz}	-0.455	0.071	0.045	0.633	1.976
β_{zzz}	-0.011	0.009	0.123	0.333	1.919
β_{total}	**0.024**	**0.022**	**0.189**	**2.208**	**9.225**

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