Supporting information for

Photovoltaic performance and the energy landscape of $CH_3NH_3PbI_3$

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Table S1. The orientation direction of different MA ions in optimised β phase structure optimised with lead fixed and relaxed, which is calculated by: Coordinate $_N$ – Coordinate $_C$.

Lead fixed					Lead relaxed			
MA vectors	MA	X	Y	Z	MA vectors	x	y	z
00-1	1	0.70	0.70	-1.11	00-1	0.66	-0.69	-1.15
	2	-0.49	-0.49	-1.31		-0.72	-0.60	-1.16
	3	-0.49	-0.49	-1.31		0.66	-0.69	-1.15
	4	0.70	0.70	-1.11		-0.67	-0.65	-1.16
	Average	0.11	0.11	-1.21		-0.01	-0.66	-1.16
-110	1	-1.03	1.06	-0.06	-1-10	-1.03	-0.95	0.48
	2	-0.76	0.98	-0.8		-0.96	-1.00	-0.54
	3	-0.72	0.70	-1.09		-1.02	-1.07	0.01
	4	-1.06	1.03	-0.1		-0.99	-1.08	0.07
	Average	-0.89	0.94	-0.52		-1.00	-1.02	0.00
11-1	1	0.88	0.96	-0.71	-1-11	-0.97	-0.88	0.72
	2	-0.57	0.76	-1.13		-1.16	0.27	0.89
	3	0.95	-0.57	-0.99		-1.09	-0.52	0.84
	4	0.75	0.73	-1.05		-1.08	-1.00	0.17
	Average	0.50	0.47	-0.97		-1.08	-0.53	0.66

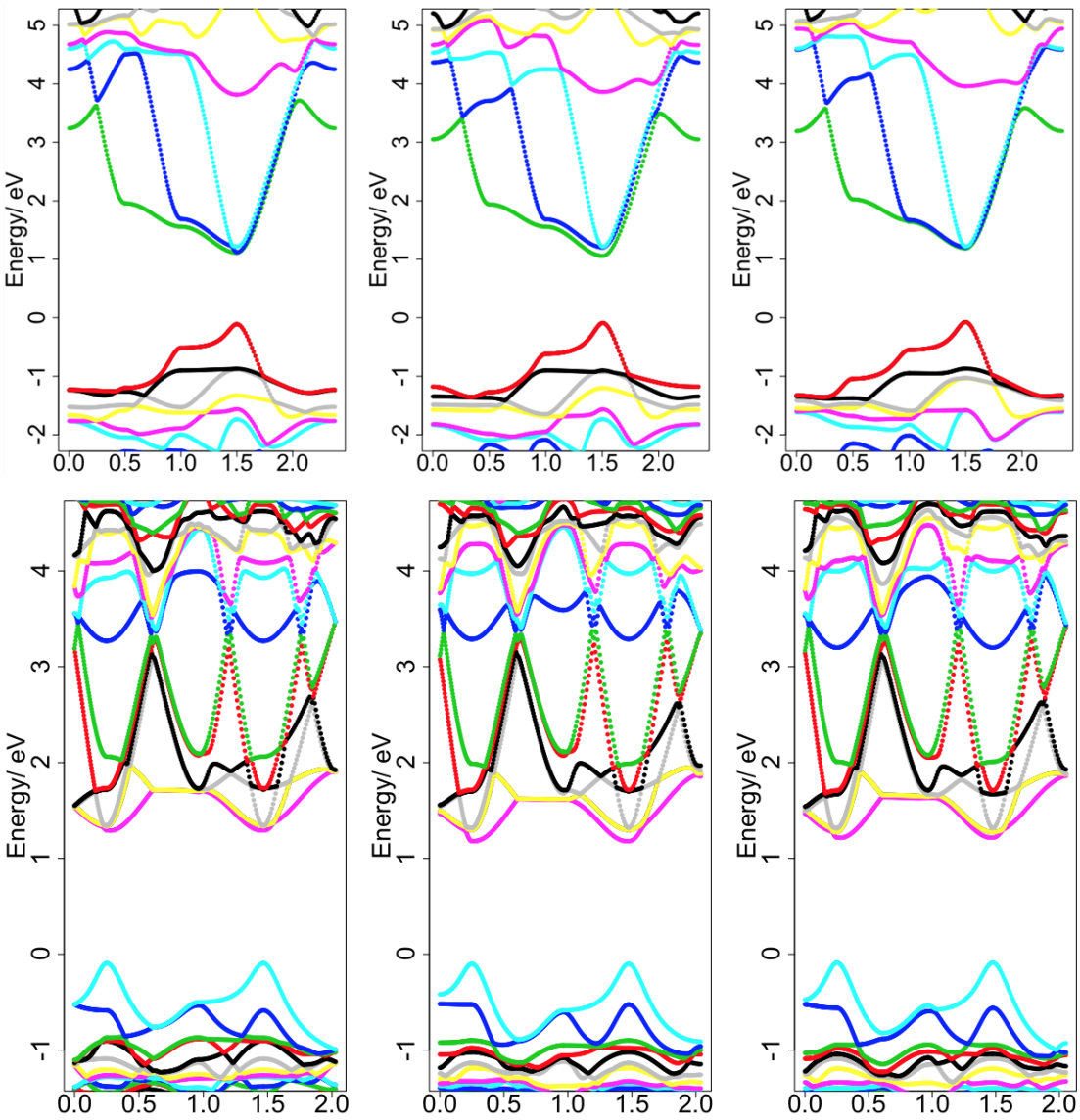

Figure S1. The band structure of the α phase and β phase with lead fixed. The upper three are the band diagrams (from left to right corresponding to 001-, 110- and 111-$MAPbI_3$, respectively) of α phase. The band diagrams of β phase are shown at lower (from left to right corresponding to 001-, 110- and 111-$MAPbI_3$, respectively).

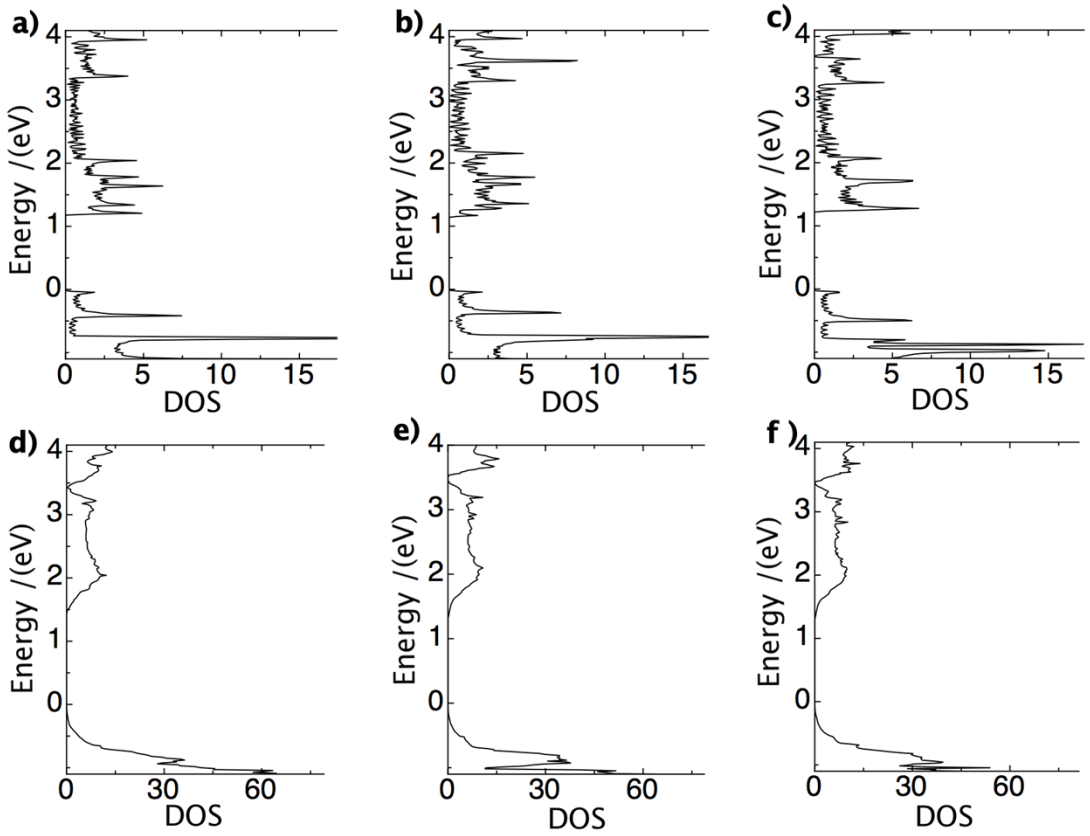

Figure S2. Density of states of the structure of lead atom relaxed. **a)**, **b)** and **c)** are DOS of α phase 001-,110-,111-$MAPbI_3$, respectively. **d)**, **e)** and **f)** are the DOS of β phase 001-,110-,111-$MAPbI_3$, respectively.

Born Charge

Born charge tensors vary as the MA ion rotate. In theoretical optimized structure, the MA ion is not at the center of the inorganic cage, carbon atoms are always closer to the cage boundary. The no-diagonal elements are close to zero. For the lead atoms, the zz component born charge reduce from 5.15 to 5.01 to 4.78, as MA ions rotate from [001] to [011] and to [111]. It is little strange for iodine ions, its born charge tensor is very big only at one component. Among those three iodine ions, one takes xx component, one takes yx component and the last one must take zz component.

Table S2. Born charges of the lead and iodine ions in different MA orientated $MAPbI_3$ unit cells. (alpha phase, lead fixed)

MA orientation (accurate direction)	ION (coordinate)	DIRECTION	X	Y	Z
001 (0.0,0.0,0.24)	lead (0.5 0.5 0.5)	X	4.688	0.007	-0.064

		Y	0.007	4.682	-0.06
		Z	-0.063	-0.059	5.146
	iodine (0.5 0.5 0)	X	-0.723	-0.007	0.035
		Y	-0.007	-0.705	0.033
		Z	-0.007	-0.009	**-4.543**
	iodine (0.5 0.0 0.5)	X	-0.905	0.01	-0.083
		Y	0.001	**-4.239**	-0.038
		Z	-0.087	0.018	-0.654
	iodine (0.0 0.5 0.5)	X	**-4.063**	-0.002	-0.033
		Y	0.009	-0.882	-0.096
		Z	0.021	-0.1	-0.659
011 (-0.01, 0.11, 0.20)	lead (0.5 0.5 0.5)	X	4.995	0.007	-0.03
		Y	0.008	4.515	0.36
		Z	-0.03	0.372	5
	iodine (0.5 0.5 0)	X	-0.801	0.012	0.01
		Y	0.008	-0.674	-0.23
		Z	0.001	-0.056	**-4.41**
	iodine (0.5 0.0 0.5)	X	-0.991	0.015	-0.01
		Y	0.022	**-4.076**	-0.05
		Z	-0.01	-0.24	-0.71
	iodine (0.0 0.5 0.5)	X	**-4.299**	0	0
		Y	0	-0.716	-0.03
		Z	0.018	-0.049	-0.74
111 (0.13 0.14, 0.13)	lead (0.5 0.5 0.5)	X	4.863	0.021	0.072
		Y	0.021	4.882	0.073
		Z	0.071	0.073	4.776
	iodine (0.5 0.5 0)	X	-0.759	-0.113	-0.018
		Y	-0.111	-0.739	-0.015
		Z	-0.032	-0.03	**-4.198**
	iodine (0.5 0.0 0.5)	X	-0.758	0.006	-0.114
		Y	-0.028	**-4.452**	-0.037
		Z	-0.109	-0.031	-0.745

	iodine (0.0 0.5 0.5)	X	**-4.246**	-0.031	-0.042
		Y	0.004	-0.742	-0.108
		Z	-0.034	-0.104	-0.749

Table S3. Born effective charge beta phase 001

(lead fixed)

ION	DIRECTION	X	Y	Z
Pb(0.00, 0.00, 0.00)	X	4.581	-0.487	0.024
	Y	0.412	4.597	0.065
	Z	0.037	0.051	5.060
Pb(0.50, 0.50, 0.50)	X	4.581	-0.487	0.024
	Y	0.412	4.597	0.065
	Z	0.037	0.051	5.060
Pb(0.00, 0.00, 0.50)	X	4.597	0.412	0.065
	Y	-0.487	4.581	0.024
	Z	0.051	0.037	5.060
Pb(0.50, 0.50, 0.00)	X	4.597	0.412	0.065
	Y	-0.487	4.581	0.024
	Z	0.051	0.037	5.060
I(0.00, 0.00, 0.25)	X	-0.696	0.035	-0.041
	Y	0.014	-0.680	0.025
	Z	-0.079	0.016	-5.398
I(0.50, 0.50, 0.75)	X	-0.696	0.035	-0.041
	Y	0.014	-0.680	0.025
	Z	-0.079	0.016	-5.398
I(0.00, 0.00, 0.75)	X	-0.680	0.014	0.025
	Y	0.035	-0.696	-0.041
	Z	0.016	-0.079	-5.398
I(0.50, 0.50, 0.25)	X	-0.680	0.014	0.025
	Y	0.035	-0.696	-0.041
	Z	0.016	-0.079	-5.398
I(0.21, 0.71, 0.00)	X	-2.569	1.767	0.099
	Y	1.767	-2.569	0.099
	Z	0.088	0.088	-0.621
I(0.79, 0.29, 0.00)	X	-2.576	1.858	-0.031
	Y	1.858	-2.576	-0.031
	Z	-0.017	-0.017	-0.602
I(0.29, 0.21, 0.00)	X	-2.665	-1.761	-0.137
	Y	-1.754	-2.459	0.009
	Z	-0.082	0.012	-0.636
I(0.79, 0.71, 0.50)	X	-2.665	-1.761	-0.137
	Y	-1.754	-2.459	0.009
	Z	-0.082	0.012	-0.636
I(0.71, 0.79, 0.00)	X	-2.459	-1.754	0.009
	Y	-1.761	-2.665	-0.137

	Z	0.012	-0.082	-0.636
I(0.21, 0.29, 0.50)	X	-2.459	-1.754	0.009
	Y	-1.761	-2.665	-0.137
	Z	0.012	-0.082	-0.636
I(0.29, 0.79, 0.50)	X	-2.576	1.858	-0.031
	Y	1.858	-2.576	-0.031
	Z	-0.017	-0.017	-0.602
I(0.71, 0.21, 0.50)	X	-2.569	1.767	0.099
	Y	1.767	-2.569	0.099
	Z	0.088	0.088	-0.621

Table S4. Born effective charge beta phase 110

(lead fixed)

ION	DIRECTION			
Pb(0.00, 0.00, 0.00)	X	4.690	0.506	0.169
	Y	-0.570	4.871	-0.033
	Z	0.138	-0.025	4.713
Pb(0.50, 0.50, 0.50)	X	4.592	0.567	0.150
	Y	-0.449	4.830	-0.012
	Z	0.127	-0.006	4.757
Pb(0.00, 0.00, 0.50)	X	4.752	-0.484	0.084
	Y	0.538	4.654	-0.100
	Z	0.082	-0.077	4.766
Pb(0.50, 0.50, 0.00)	X	4.824	-0.604	0.073
	Y	0.484	4.765	-0.100
	Z	0.087	-0.091	4.687
I(0.00, 0.00, 0.25)	X	-0.688	-0.141	-0.178
	Y	-0.119	-0.790	-0.002
	Z	-0.112	-0.007	-4.909
I(0.50, 0.50, 0.75)	X	-0.786	-0.093	-0.176
	Y	-0.062	-0.606	0.006
	Z	-0.120	-0.017	-5.007
I(0.00, 0.00, 0.75)	X	-0.653	-0.079	-0.060
	Y	-0.112	-0.733	0.129
	Z	0.010	0.099	-5.053
I(0.50, 0.50, 0.25)	X	-0.771	-0.104	-0.001
	Y	-0.127	-0.727	0.136
	Z	0.063	0.107	-4.905
I(0.21, 0.71, 0.00)	X	-2.821	1.958	0.048
	Y	1.932	-2.601	0.060
	Z	-0.001	0.100	-0.612
I(0.79, 0.29, 0.00)	X	-2.644	1.979	-0.023
	Y	2.037	-2.812	0.015
	Z	-0.082	0.052	-0.624
I(0.29, 0.21, 0.00)	X	-2.530	-1.931	-0.111

	Y	-1.969	-2.561	0.100
	Z	-0.141	0.084	-0.811
I(0.79, 0.71, 0.50)	X	-2.526	-1.903	-0.087
	Y	-1.926	-2.562	0.052
	Z	-0.102	0.065	-0.812
I(0.71, 0.79, 0.00)	X	-2.626	-1.990	-0.004
	Y	-1.987	-2.628	0.016
	Z	-0.024	-0.016	-0.645
I(0.21, 0.29, 0.50)	X	-2.640	-1.998	-0.009
	Y	-2.030	-2.667	-0.002
	Z	-0.026	-0.011	-0.639
I(0.29, 0.79, 0.50)	X	-2.490	1.839	-0.061
	Y	1.868	-2.717	-0.082
	Z	-0.146	-0.058	-0.630
I(0.71, 0.21, 0.50)	X	-2.700	1.846	0.073
	Y	1.873	-2.530	0.047
	Z	0.062	0.134	-0.627

Table S5. Born effective charge beta phase 111

(lead fixed)

ION	DIRECTION	X	Y	Z
Pb(0.00, 0.00, 0.00)	X	4.688	0.652	-0.203
	Y	-0.366	4.734	-0.063
	Z	-0.186	-0.073	4.832
Pb(0.50, 0.50, 0.50)	X	4.668	0.503	-0.163
	Y	-0.483	4.632	-0.076
	Z	-0.182	-0.034	4.953
Pb(0.00, 0.00, 0.50)	X	4.634	-0.504	-0.130
	Y	0.494	4.722	-0.145
	Z	-0.125	-0.121	4.865
Pb(0.50, 0.50, 0.00)	X	4.683	-0.375	-0.143
	Y	0.652	4.701	-0.142
	Z	-0.111	-0.149	4.943
I(0.00, 0.00, 0.25)	X	-0.831	0.018	0.075
	Y	0.043	-0.633	0.060
	Z	0.025	0.017	-5.110
I(0.50, 0.50, 0.75)	X	-0.683	0.001	0.126
	Y	0.035	-0.691	0.170
	Z	0.030	0.081	-5.339
I(0.00, 0.00, 0.75)	X	-0.781	-0.021	0.121
	Y	-0.074	-0.617	0.052
	Z	0.051	0.026	-5.159
I(0.50, 0.50, 0.25)	X	-0.609	0.057	0.179
	Y	0.034	-0.834	0.077
	Z	0.054	0.027	-5.229
I(0.21, 0.71, 0.00)	X	-2.621	1.838	0.154

	Y	1.830	-2.503	0.060
	Z	0.215	0.059	-0.691
I(0.79, 0.29, 0.00)	X	-2.445	1.735	-0.016
	Y	1.761	-2.641	-0.111
	Z	-0.017	-0.184	-0.611
I(0.29, 0.21, 0.00)	X	-2.829	-2.033	-0.057
	Y	-1.986	-2.666	0.056
	Z	-0.001	0.110	-0.574
I(0.79, 0.71, 0.50)	X	-2.646	-1.809	-0.050
	Y	-1.835	-2.496	0.031
	Z	-0.028	0.110	-0.664
I(0.71, 0.79, 0.00)	X	-2.601	-1.913	-0.003
	Y	-1.984	-2.731	0.026
	Z	0.062	0.092	-0.677
I(0.21, 0.29, 0.50)	X	-2.524	-1.888	0.081
	Y	-1.894	-2.703	-0.128
	Z	0.174	-0.093	-0.588
I(0.29, 0.79, 0.50)	X	-2.728	1.921	-0.066
	Y	1.897	-2.569	0.009
	Z	-0.095	0.006	-0.612
I(0.71, 0.21, 0.50)	X	-2.500	1.804	0.045
	Y	1.855	-2.681	0.114
	Z	0.048	0.140	-0.698

Estimation of the hindering field($\mathbf{E}_0$) and the screen field in Tress' experiment. For the scanning rate of 1,000 meV/s, at the voltage of 0.65 V, the current are 15.72 mA/cm^2 and 9.04 mA/cm^2, from Figure 1a. The thickness of solar cell is about 300 nm, hence, the field can estimated as

$$\mathbf{E}_0 = 0.65V/300nm = 2.17 \times 10^6\ V/m.$$

If we assuming there is no power lost, the power of circuit are the same:

$$V * I_+ + V_s * I_+ = V * I_-$$

Where $_-$ and $_+$ is for the backward and forward measurement. V_s is the potential produced by the screen field. Then,

$$V_s = V * \frac{I_- - I_+}{I_+} = 0.65 * 0.74\ V = 0.48\ V$$

Therefore the screen field is $E_s = V_s/d = 0.48\ V/300\ nm = 1.6 \times 10^6$ V/m. The total field is $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_s = 5.67 \times 10^5$ V/m. Energies of the polarised MA^+ ions along six directions are $|\mathbf{M}||\mathbf{E}|$, zero and $-|\mathbf{M}||\mathbf{E}|$, respectively. The Boltzmann ratios are estimated as $\exp(2|\mathbf{M}||\mathbf{E}|/kT) : 4 \times \exp(|\mathbf{M}||\mathbf{E}|/kT) : 1.00 = 1.005 : 4 \times 1.009 : 1.00$. The net percentage of the polarised MA^+ ions is about $\frac{1.005-1.00}{1.005+4\times1.02+1} = 0.08\%$. The net polarised charge density ρ is the totally polarised charge density multiplying its polarisation percentage, about 6.4 μC/cm^2 × 0.08 % = 0.0048 μC/cm^2. In a parallel-plate capacitor, for this charge density on the two plate, the field in it can be estimated as $\mathbf{E}_p = \rho/\varepsilon_0\varepsilon_r = 2.58 \times 10^5$ V/m.

Calculation method selection:

Some theoretical calculations show that van der Walls (vdW) force is very important in hybrid perovskite calculations.[1] It is believed to be. But all of the list works are calculated on the level of PBE. They show that PBE+vdW method is better than PBE method. While we use PBE revised for solid, which is a function with improved description for solid. There are four papers using PBEsol without vdW.[2] We will show below that PBEsol is better than other methods with vdW.

As shown in below Table S6, the sequence of lattice parameters and volumes estimated by various methods is:

PBE > optPBE-vdW > optB86b-vdW > PBE-vdw > PBEsol > EXP > PBEsol-vdw.

Parameters calculated by PBEsol are the closest parameters to experiment. If we consider the thermal expansion, lattice parameters get smaller. Hence, PBEsol is better than optB86b-vdW, optPBE-vdW and PBE-vdW.

Table S6. Lattice parameters of tetragonal (β) phase $MAPbI_3$ calculated by various methods.

Method	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
PBE	9.074	9.029	13.175	1078.800
optPBE-vdW[1]	9.007	9.015	13.010	1056.360
optB86b-vdW[1]	8.891	8.869	12.811	1010.130
PBE-vdW[2]	8.868	8.802	12.806	999.549
PBEsol	8.880	8.816	12.723	995.723
Exp[3]	8.855	8.855	12.659	992.600
Exp[4]	8.849	8.849	12.642	990.000
Exp[5]	8.860	8.860	12.453	975-987
PBEsol-vdW[2]	8.544	8.642	12.048	888.578

[1] is the vdW-DF functional of Langreth and Lundqvist et al. (M. Dion, H. Rydberg, E. Schr¨oder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92 , 246401 (2004).;J. Klime˘s, D. R. Bowler, and A. Michaelides, Phys. Rev. B 83 , 195131 (2011).)

[2]is the DFT-D2 method of Grimme. (S. Grimme, J. Comp. Chem. 27, 1787 (2006).X. Wu, M. C. Vargas, S. Nayak, V. Lotrich, and G. Scoles, J. Chem. Phys. 115, 8748 (2001).)

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Table S7. Lattice parameters of orthorhombic (γ) phase $MAPbI_3$ calculated by various methods.

Method	*a* (Å)	*b* (Å)	*c* (Å)	*V* (*Å*^{3})
PBE	9.075	12.838	8.698	1013.250
optPBE-vdW	8.980	12.821	8.699	1001.480
Exp3	8.861	12.620	8.581	959.500
optB86b+vdW	8.853	12.059	8.557	959.101
Exp2	8.836	12.580	8.555	951.010
PBEsol	8.855	12.573	8.474	943.523
PBE-vdW	8.707	12.579	8.522	933.338
PBEsol+vdW	8.435	12.256	8.388	867.038
PBE[6]	9.226	12.876	8.619	1023.880
optB86b+vdW[6]	8.831	12.648	8.570	957.180

[6] Y. Wang, T. Gould, J.F. Dobson, H. Zhang, H. Yang, X. Yao, and H. Zhao, Phys. Chem. Chem. Phys. **16**, 1424 (2014).

Table S7 shows the geometry parameters of the orthorhombic phase unit cell after with different method optimised. We employ PBE and optB86b+vdW methods as ref Wang did.[6] Our calculations obtained geometries are closer to the experiment than Wang get. Both optB86b+vdW and PBEsol give good agreement. If we take the Exp3 as standard, then optB86b+vdw gives better results in volume, but it gives a shorter *b* cell vector, its error is 0.57 *Å*. The largest difference for PBEsol is *c* cell vector, its error is only 0.11 *Å*. That's to say, PBEsol gives a better shape. If we set the recent result Exp2 as standard, PBEsol gives better results both in volume and shape. In general, the PBEsol method is better than optB86b+vdW, PBE+vdW, or optPBE+vdW.

Reference:

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