Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Defects in crystalline PVDF: a Density Functional Theory – Density Functional Tight Binding study

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Table S1. Structural parameters of α, β, γ, and δ phases of PVDF with different computational schemes. Relative differences Δ of computed cell vectors from the experimental values of Ref. [1] are also given.

		DFT (PBE)								DFTB (equivalent cell sizes with respect to DFT models)								DFT PBE0/ cc-pVTZ[2]		Exp.[1,3]
		SIESTA vdW-D2		VASP No-dispersion		VASP vdW-D3		VASP vdW-D2		30b-3-1 UFF		30b-3-1 no dispersion		PBC-0-3 UFF		PBC-0-3 no dispersion				
phase		*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å	Δ,%	*abc*, Å
α	a	4.82	2.92	5.04	1.53	5.02	1.27	5.02	1.27	4.91	1.10	4.90	1.23	4.89	1.46	4.80	3.26	5.03	1.39	4.96
	b	9.24	4.11	9.67	0.34	9.59	0.48	9.59	0.48	9.33	3.23	9.29	3.64	9.11	5.50	9.05	6.15	9.98	3.49	9.64
	c	4.64	0.36	4.68	1.34	4.69	1.48	4.69	1.48	4.79	3.73	4.71	2.02	4.71	1.92	4.64	0.35	4.65	0.56	4.62
β	a	8.45	1.55	8.69	1.24	8.69	1.23	8.69	1.23	8.38	2.31	8.34	2.82	8.36	2.57	8.07	5.92	8.69	1.29	8.58
	b	4.59	6.60	4.94	0.51	4.93	0.51	4.93	0.51	4.69	4.47	4.63	5.71	4.63	5.70	4.52	7.88	4.89	0.35	4.91
	c	2.57	0.21	2.59	0.98	2.59	0.98	2.59	0.98	2.63	2.85	2.60	1.44	2.59	1.14	2.56	0.06	2.57	0.31	2.56
δ	a	5.00	0.82	5.01	1.08	4.98	0.33	4.98	0.33	4.88	1.58	5.00	0.89	4.83	2.65	4.83	2.70	4.83	2.64	4.96
	b	9.11	5.82	9.71	0.46	9.67	0.04	9.67	0.04	9.30	3.79	9.17	5.19	9.16	5.33	9.08	6.09	9.57	1.05	9.67
	c	9.29	0.98	9.32	1.32	9.31	1.19	9.31	1.18	9.51	3.34	9.36	1.76	9.35	1.68	9.20	0.04	9.23	0.28	9.20
γ	a	4.83	2.65	4.96	0.08	4.86	2.00	4.86	2.00	4.91	0.99	4.87	1.86	4.82	2.74	4.77	3.85	5.01	1.03	4.96
	b	9.04	6.23	9.59	0.50	9.29	3.68	9.29	3.68	9.06	6.04	9.27	3.84	8.98	6.88	9.06	6.06	10.00	3.72	9.64
	c	4.63	0.31	4.68	1.37	4.66	0.96	4.66	0.96	4.80	3.87	4.71	1.89	4.71	1.94	4.64	0.35	4.65	0.54	4.62

Table S2. The bandgap of crystal α phase and β phase of PVDF obtained with different methods (in eV) compared with available experimentally measured value for β Phase.

Phase	DFT (B3LYP)	DFT (PBE)	DFTB (3ob-3-1)	Experiment
α	9.10	7.09	11.45	-
β	7.23	5.93	10.48	6.5[4]

References

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