

Structure-related bandgap of hybrid lead halide perovskites and close-packed APbX₃ family of phases

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Supporting information

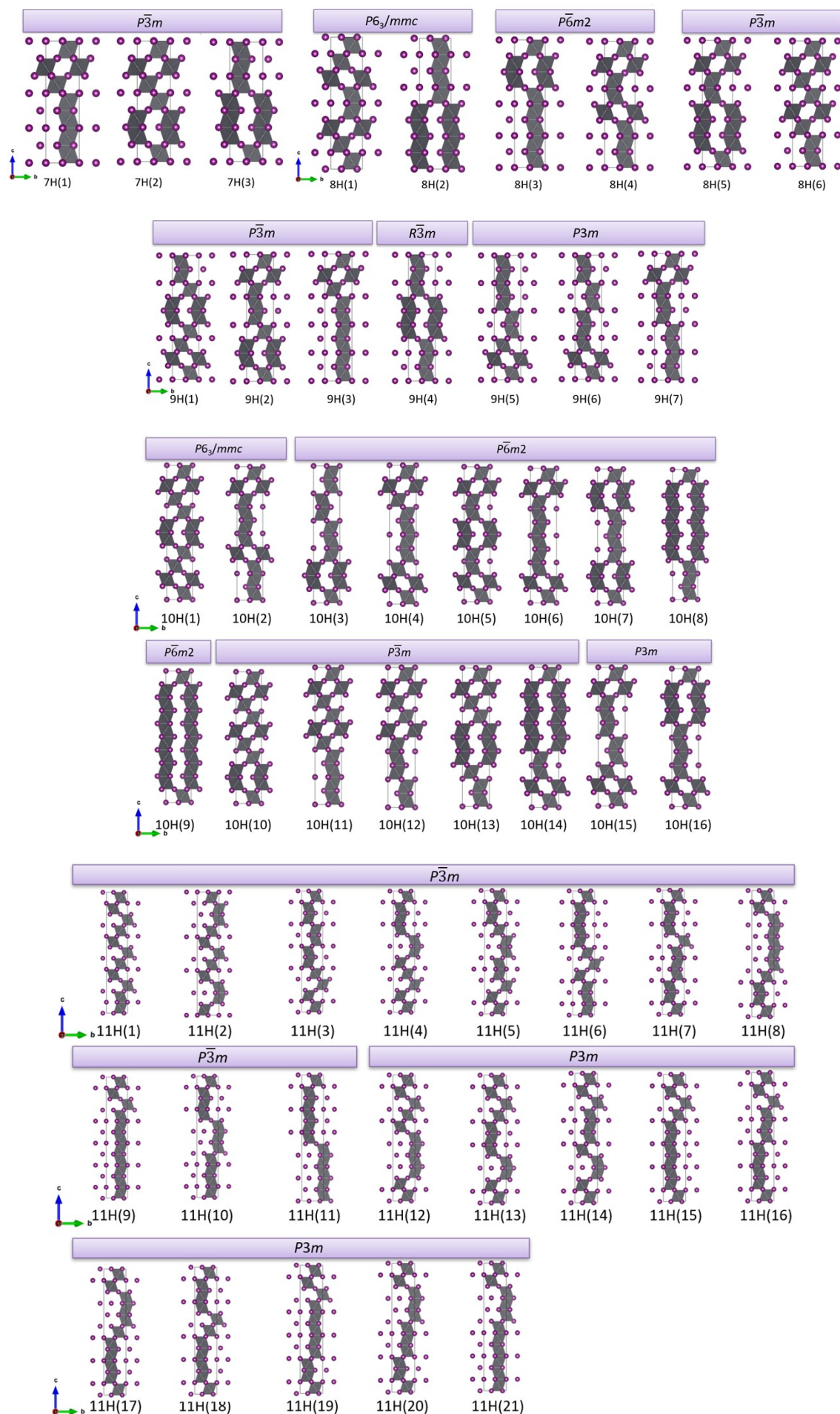


Figure S1. Constructed all possible 7H, 8H 9H, 10H and 11H close-packed polytypes of APbI_3 .

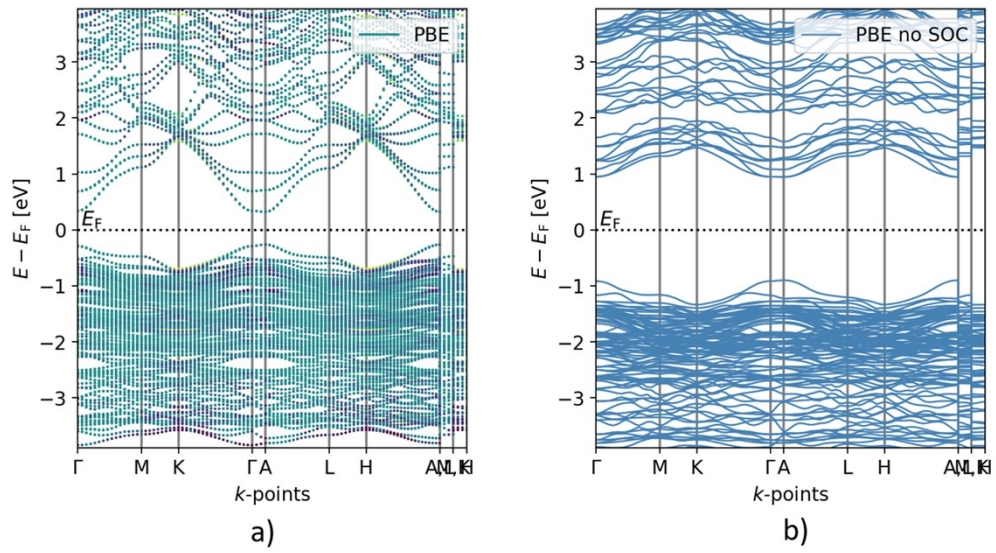


Figure S2. Band structure of the 9H(1) polytype computed at the PBE+SOC (a) and PBE (b) levels of theory.

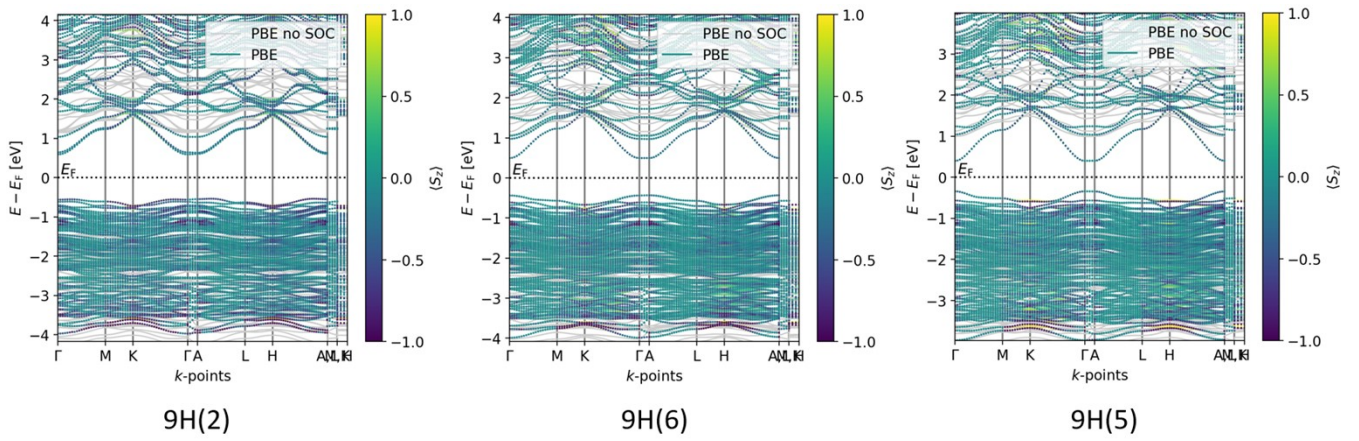


Figure S3. The band structures of 9H polytypes with different proportion of h and c close-packed layers. Gray color shows calculations without SOC, color shows results of calculations with SOC.

Table S1. Characteristics of possible configurations of close packings from 2 to 9 layers for APbI₃.

A number of layers in close packing	ABC symbol	Space group symmetry of the close packing	Space group symmetry of structures occupied octahedral voids by lead ions	Fraction of closed-packed layers where PbI ₆ octahedra connected by vertices
10H(1)	(ABCABCACB)	hccccccc	$D_{6h}^4 (P6_3/mmc)$	0.8
10H(2)	(ABABCACACB)	hhhchhhcc	$D_{6h}^4 (P6_3/mmc)$	0.4
10H(3)	(ABCBABACAB)	hchchhchch	$D_{3h}^1 (P\bar{6}m2)$	0.4
10H(4)	(ABCABABACB)	hccchhhccc	$D_{3h}^1 (P\bar{6}m2)$	0.6
10H(5)	(ABCACBCACB)	hcchchchcc	$D_{3h}^1 (P\bar{6}m2)$	0.6
10H(6)	(ABCACACACB)	hcchhhhhcc	$D_{3h}^1 (P\bar{6}m2)$	0.4
10H(7)	(ABCBABABCB)	hchchhhchc	$D_{3h}^1 (P\bar{6}m2)$	0.4
10H(8)	(ABABCBCBCB)	hhhchhhhhc	$D_{3h}^1 (P\bar{6}m2)$	0.2
10H(9)	(ABCBCBCBCB)	hchhhhhhhc	$D_{3h}^1 (P\bar{6}m2)$	0.2
10H(10)	(ABCABCACB)	hccccccc	$D_{3d}^3 (P\bar{3}m)$	0.8
10H(11)	(ABABCACACB)	hhhccccccc	$D_{3d}^3 (P\bar{3}m)$	0.6
10H(12)	(ABACACACB)	hhchcccc	$D_{3d}^3 (P\bar{3}m)$	0.6
10H(13)	(ABACBCACB)	hchchcccc	$D_{3d}^3 (P\bar{3}m)$	0.6
10H(14)	(ABCACBCBCB)	hcchchhhc	$D_{3d}^3 (P\bar{3}m)$	0.4
10H(15)	(ABCABACACB)	hccchchcc	$C_{3v}^1 (P3m)$	0.6
10H(16)	(ABCACACBCB)	hcchhhchc	$C_{3v}^1 (P3m)$	0.4
11H(1)	(ABCABCACBC)	hcccccccch	$D_{3d}^3 (P\bar{3}m)$	0.82
11H(2)	(ACBCABCACB)	cchccccchc	$D_{3d}^3 (P\bar{3}m)$	0.82
11H(3)	(ACBCACBCACB)	cchchchchcc	$D_{3d}^3 (P\bar{3}m)$	0.64
11H(4)	(ABCABCACAB)	hccccchch	$D_{3d}^3 (P\bar{3}m)$	0.64

11H(5)	(ACABACBACB)	chchccchhc	$D_{3d}^3 (p\bar{3}m)$	0.64
11H(6)	(ACBCBCACACB)	cchhhchhhcc	$D_{3d}^3 (p\bar{3}m)$	0.45
11H(7)	(ACACBCACBCB)	chhchchchhc	$D_{3d}^3 (p\bar{3}m)$	0.45
11H(8)	(ABACBCACBAB)	hhcchcchh	$D_{3d}^3 (p\bar{3}m)$	0.45
11H(9)	(ABABACBABAB)	hhhhccchhh	$D_{3d}^3 (p\bar{3}m)$	0.27
11H(10)	(ABACACBCBAB)	hhchhchhch	$D_{3d}^3 (p\bar{3}m)$	0.27
11H(11)	(ACACACBCBCB)	chhhhchhhhc	$D_{3d}^3 (p\bar{3}m)$	0.27
11H(12)	(ABCACACBACB)	hcchhhcccc	$C_{3v}^1 (P3m)$	0.64
11H(13)	(ABCACBCBACB)	hcchchcccc	$C_{3v}^1 (P3m)$	0.64
11H(14)	(ABCACBABACB)	hcchcchccc	$C_{3v}^1 (P3m)$	0.64
11H(15)	(ABCBCBCBACB)	hchhhhcccc	$C_{3v}^1 (P3m)$	0.45
11H(16)	(ABCBCBABACB)	hchhhchccc	$C_{3v}^1 (P3m)$	0.45
11H(17)	(ABCBCBACACB)	hchhhcchcc	$C_{3v}^1 (P3m)$	0.45
11H(18)	(ABCBCBACBCB)	hchhhccchhc	$C_{3v}^1 (P3m)$	0.45
11H(19)	(ABCBABABACB)	hchchhhccc	$C_{3v}^1 (P3m)$	0.45
11H(20)	(ABCBABACACB)	hchchchhcc	$C_{3v}^1 (P3m)$	0.45
11H(21)	(ACACACBCBCB)	chhhhchhhhc	$C_{3v}^1 (P3m)$	0.27

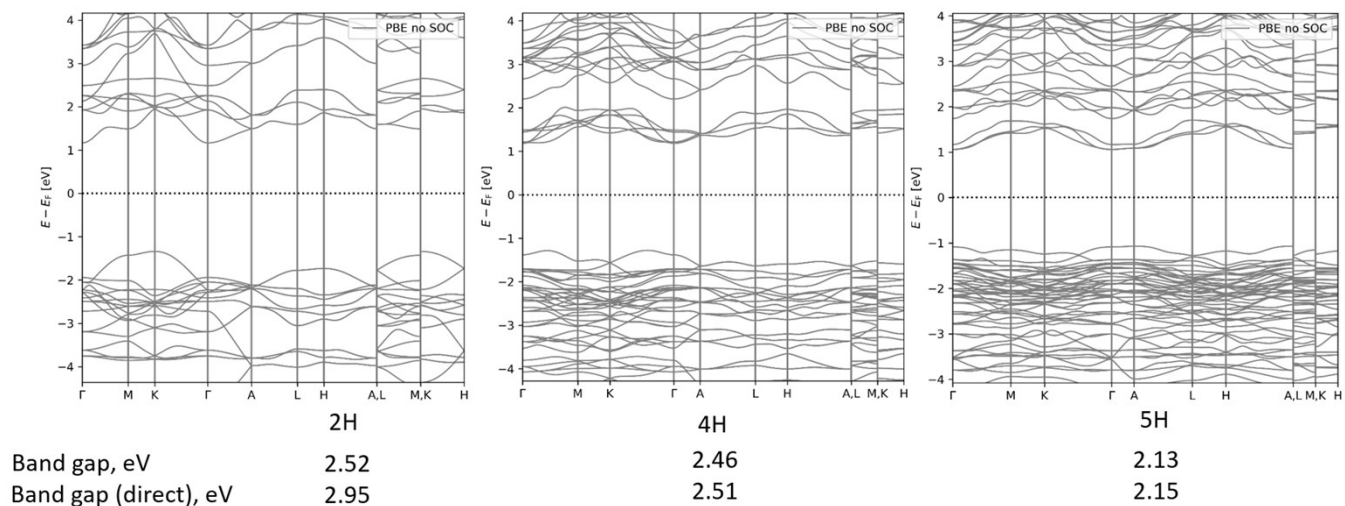


Figure S4. Calculated band structure without SOC for possible 2H, 4H and 5H polytypes of APbI₃.

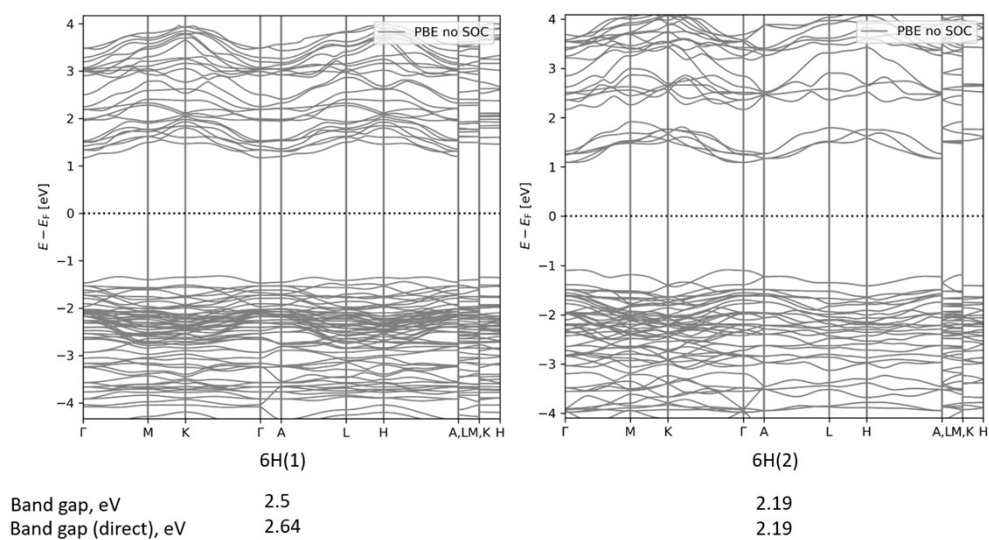


Figure S5. Calculated band structure without SOC for possible 6H polytypes of APbI₃.

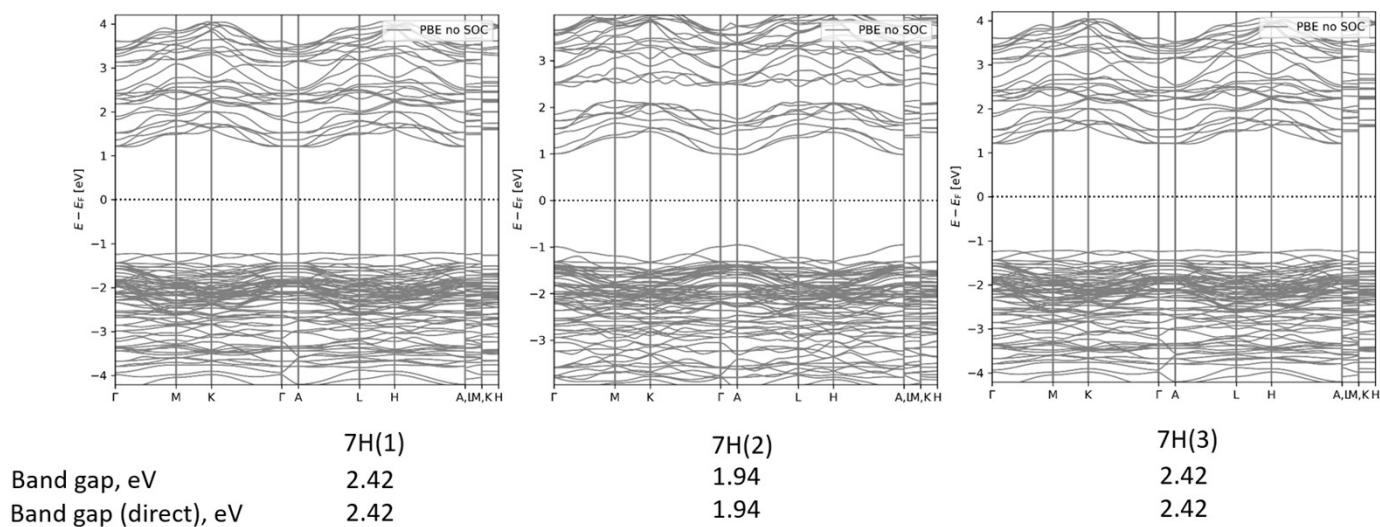


Figure S6. Calculated band structure without SOC for possible 7H polytypes of APbI₃.

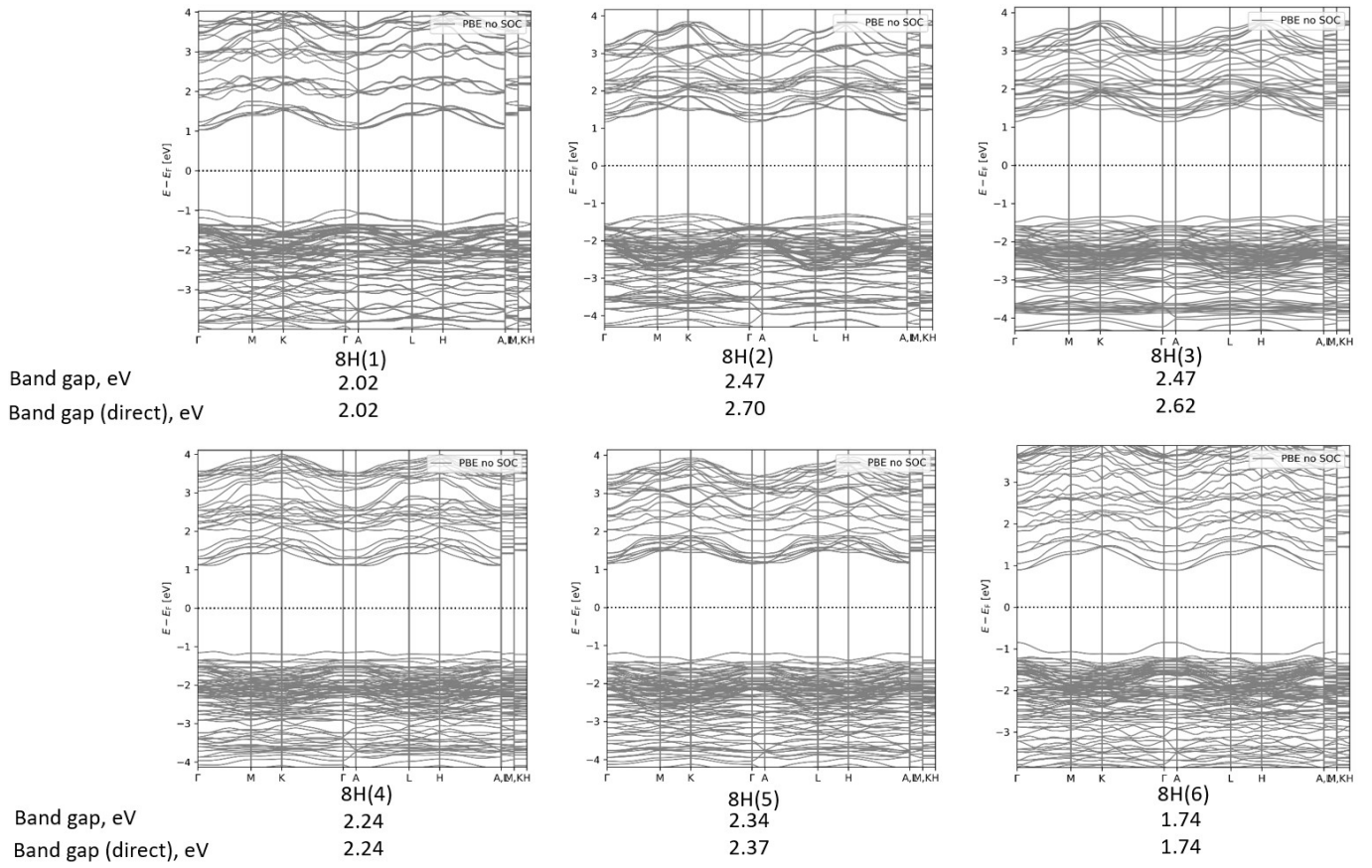


Figure S7. Calculated band structure without SOC for possible 8H polytypes of APbI₃.

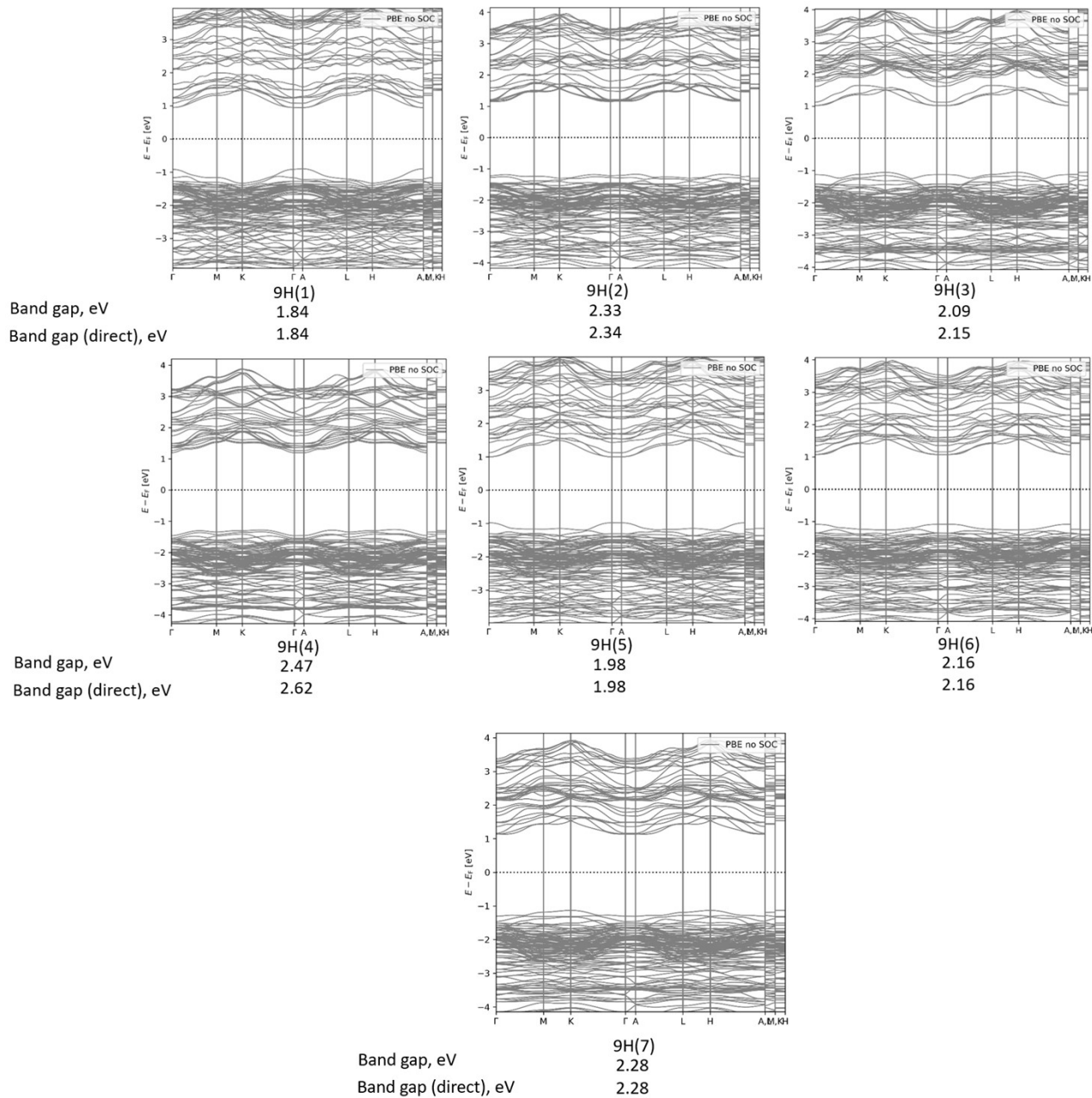


Figure S8. Calculated band structure without SOC for possible 9H polytypes of APbI₃.

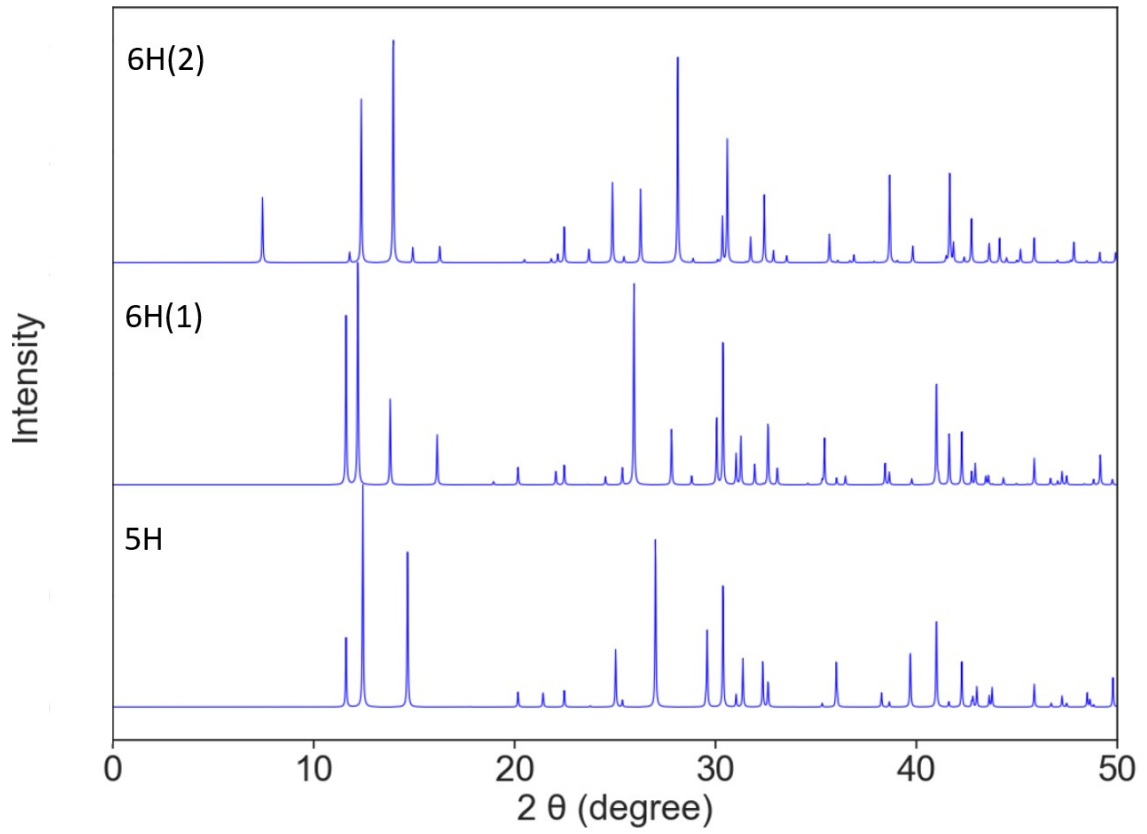


Figure S9. Calculated XRD pattern for 5H and 6H polytypes.

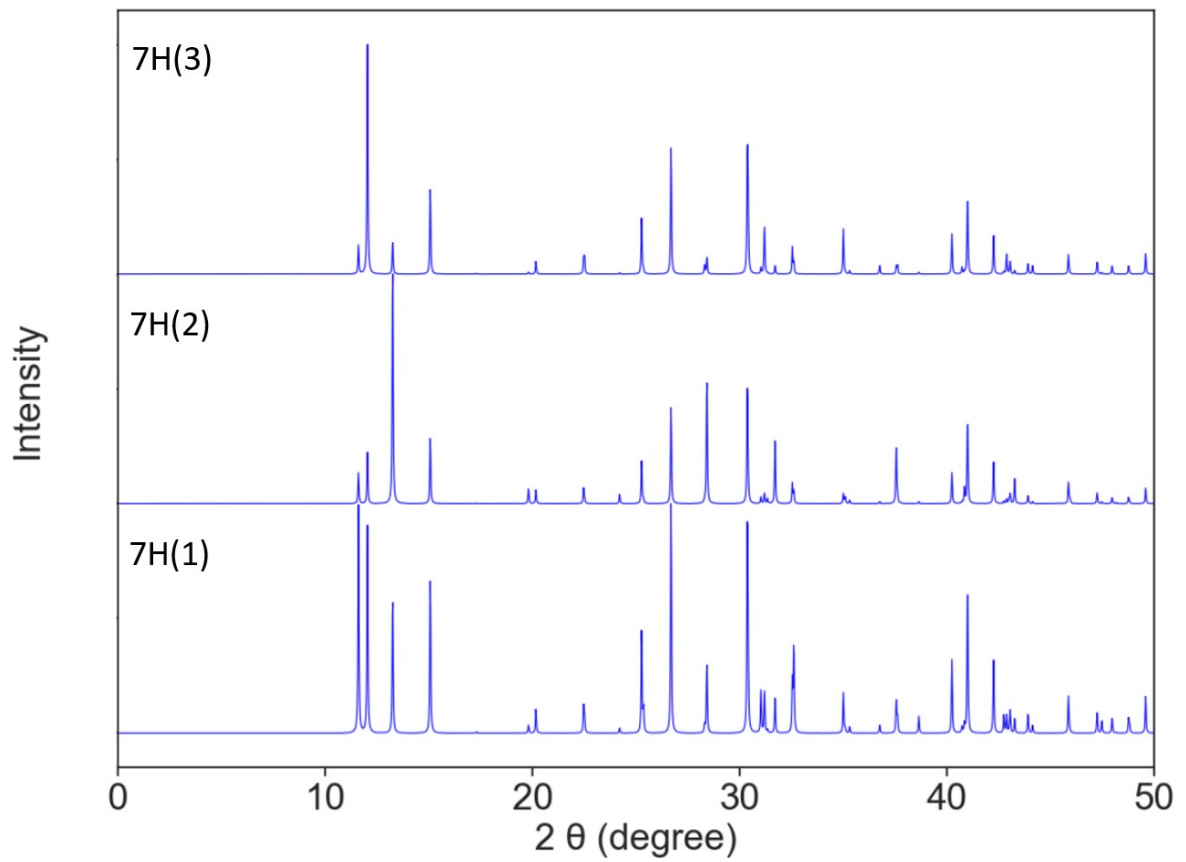


Figure S10. Calculated XRD pattern for 7H polytypes.

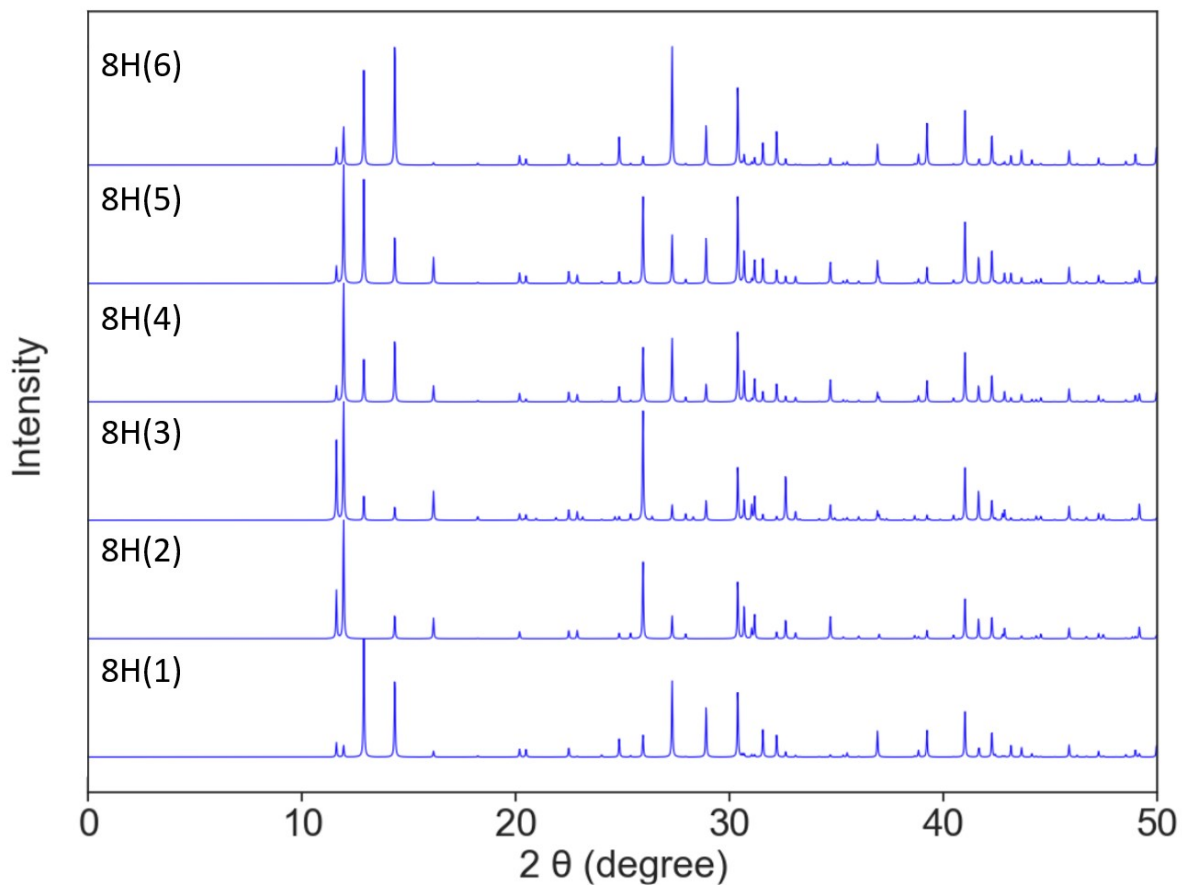


Figure S11. Calculated XRD pattern for 8H polytypes.

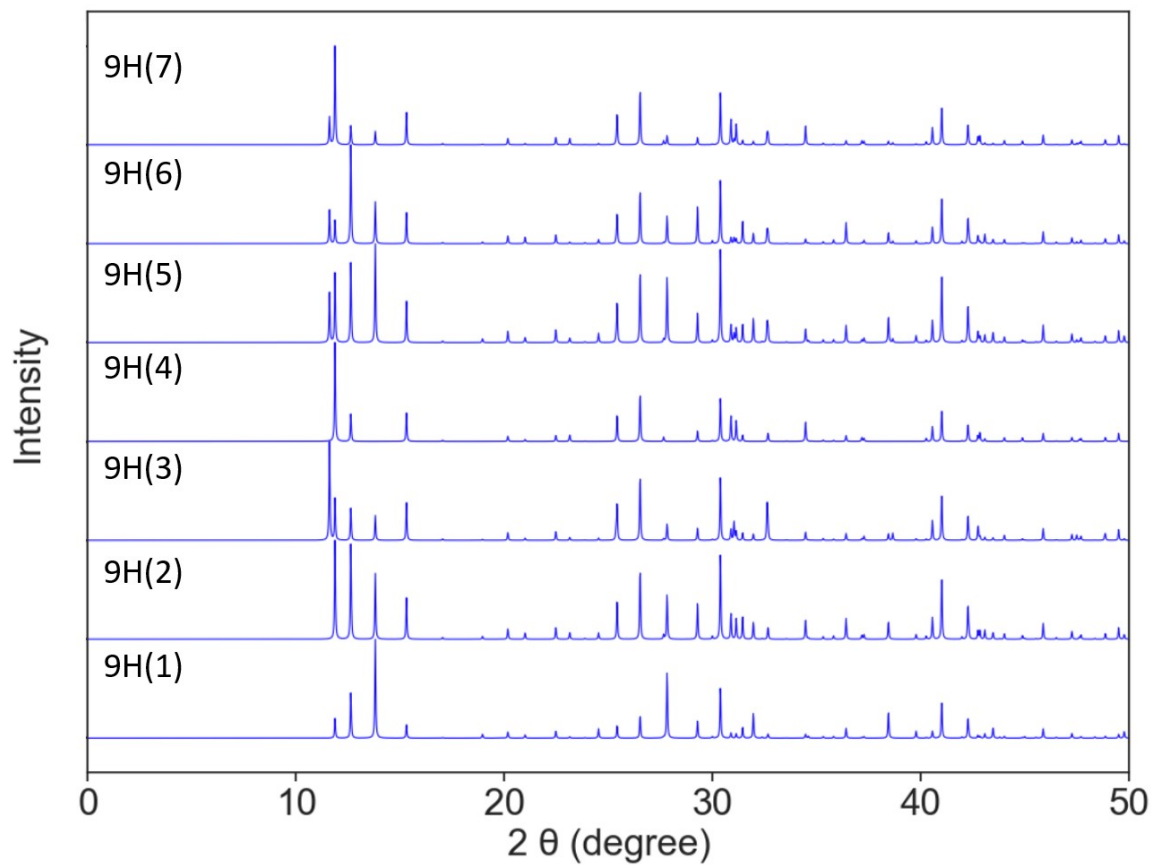


Figure S12. Calculated XRD pattern for 9H polytypes.

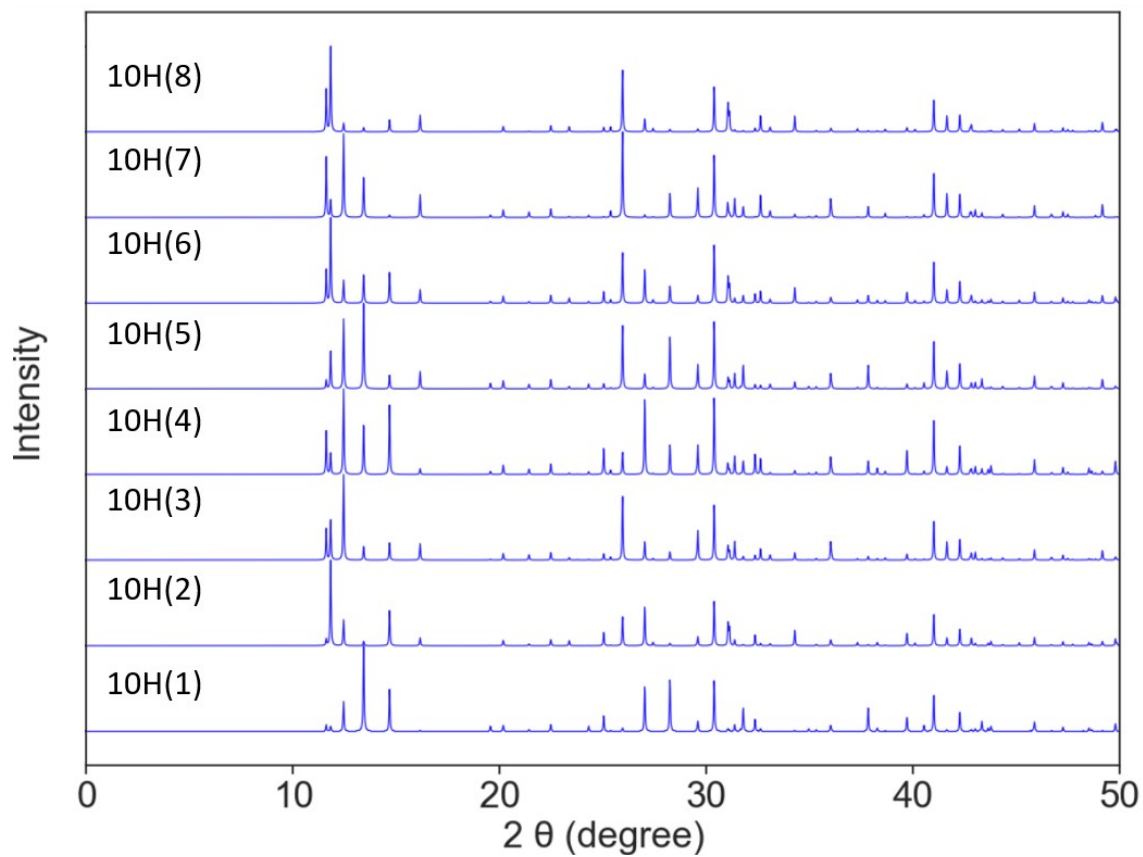


Figure S13a. Calculated XRD pattern for 10H (1-8) polytypes.

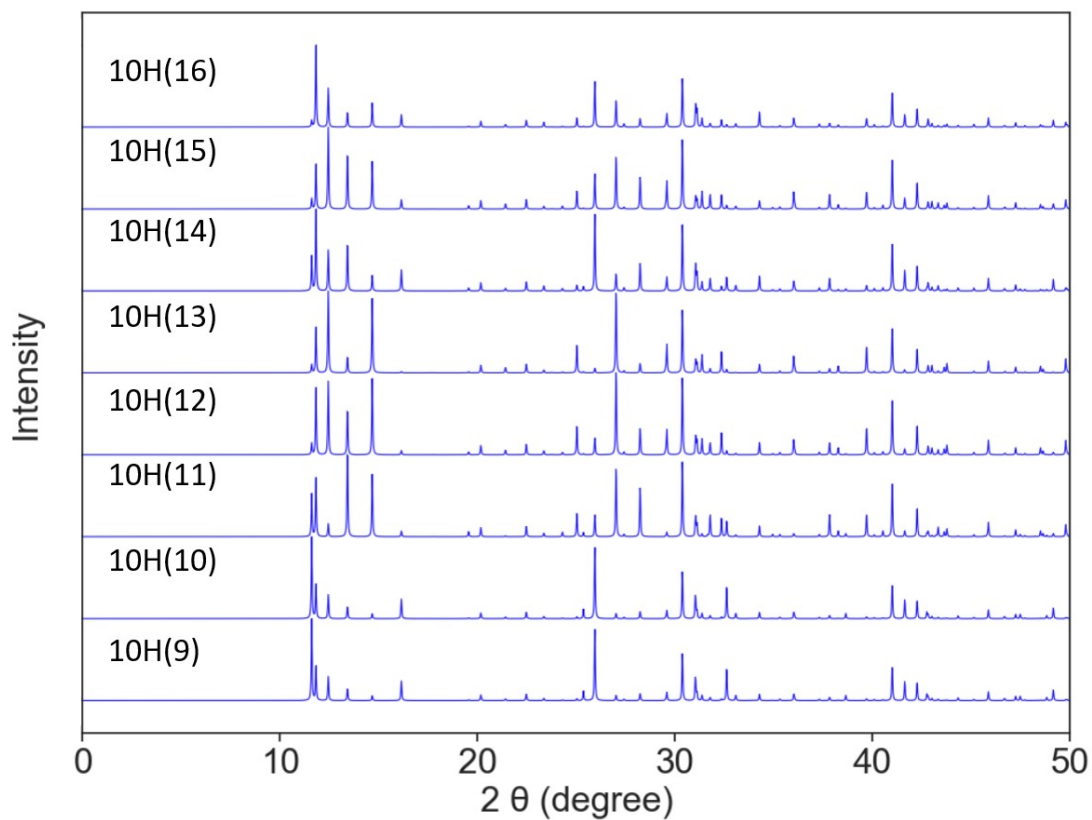


Figure S13b. Calculated XRD pattern for 10H (9-16) polytypes.

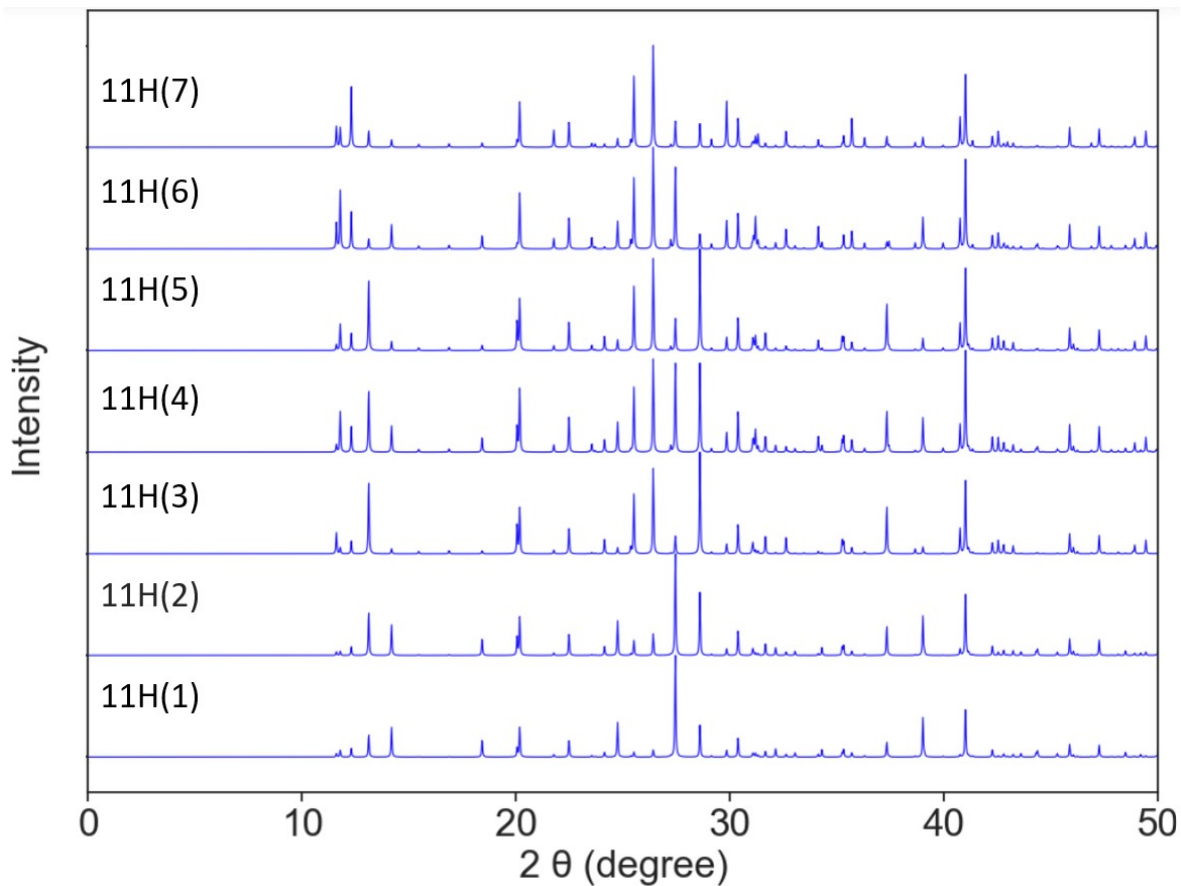


Figure S14a. Calculated XRD pattern for 11H (1-7) polytypes.

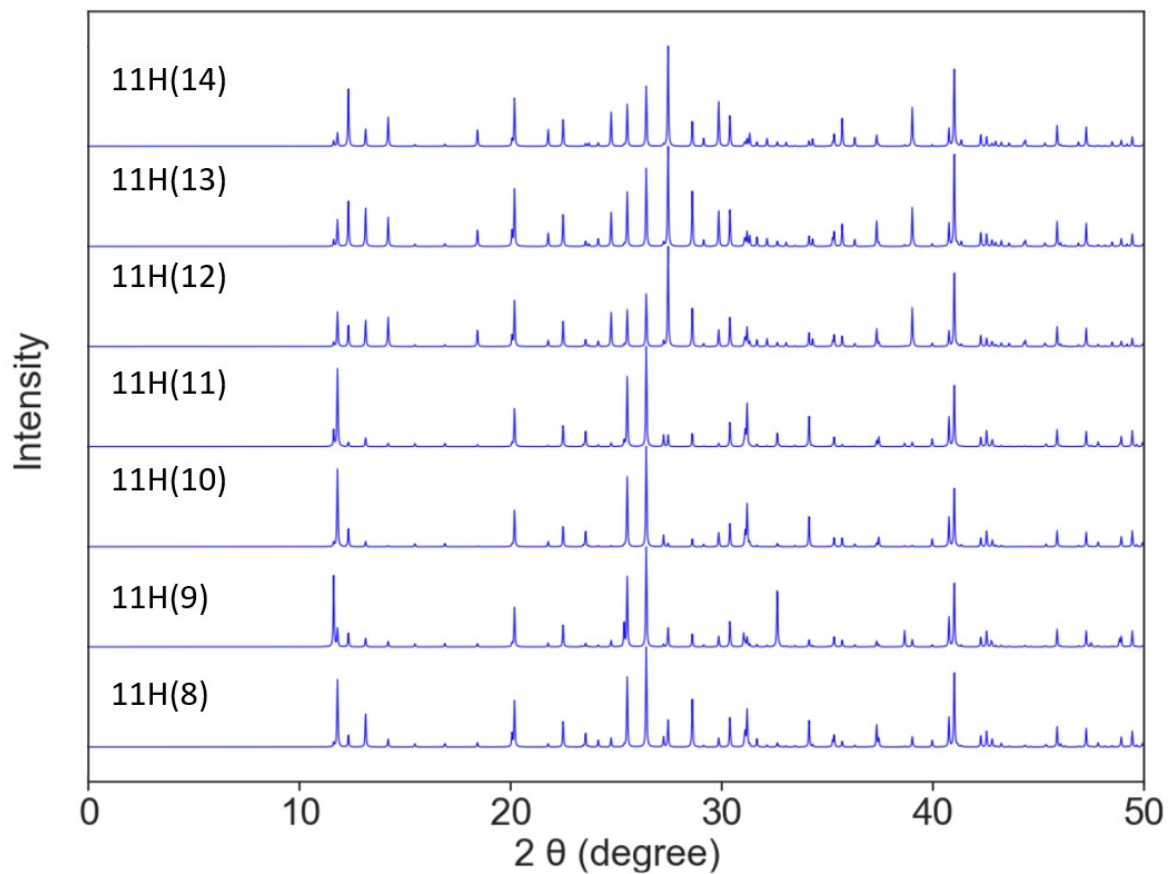


Figure S14b. Calculated XRD pattern for 11H (8-14) polytypes.

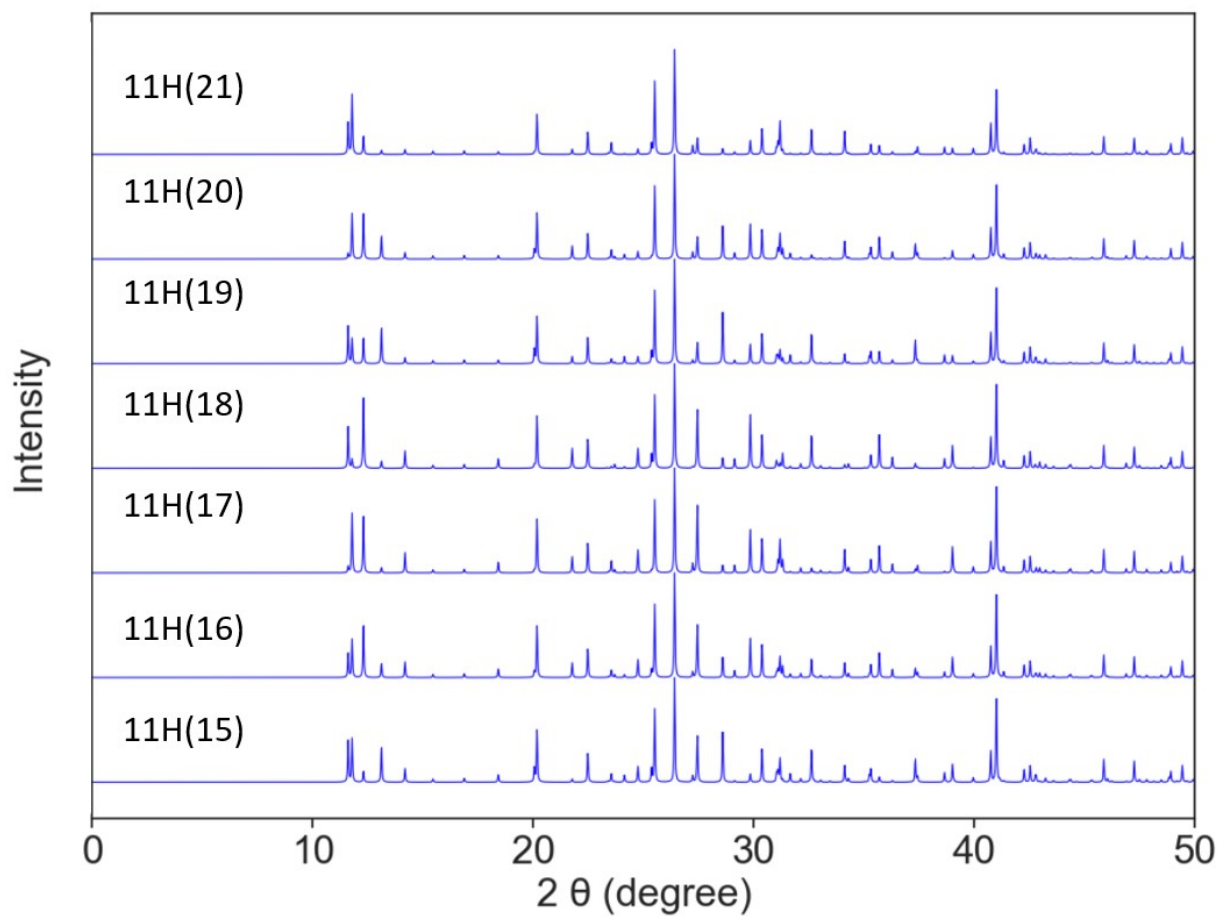


Figure S14c. Calculated XRD pattern for 11H (15-21) polytypes.