

Structural and Electronic Properties of Metal Halide Perovskites using Non-Periodic Calculations: A Combined xTB, DFT, and ONIOM Framework

Adrián Moro-Marín,^a Gregorio García,^{a,*} Silverio Coco,^a

^aIU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain).

Corresponding author: gregorio.garcia@uva.es (GG)

Supporting Information

Table SI. Pb-I distances (d_{Pb-I}) for cluster 1-1-1 optimized using the GFN2-xTB method. For bond labels, refer to figure to the right.

Label	d_{Pb-I} (Å)
1	3.63
2	2.90
3	3.55
4	2.83
5	3.77
6	3.23
7	2.92
8	2.90
9	2.89
10	4.19
11	3.25
12	2.92
13	2.90
14	2.89
15	4.13
16	2.94
17	3.38
18	2.87
19	2.84
20	3.77
21	2.93
22	2.86
23	3.08
24	3.60
25	2.83
26	2.99
27	3.17
28	2.90
29	4.81
30	2.83
31	2.95
32	3.18
33	3.58
34	2.97
35	3.78
36	4.15
37	2.92
38	3.13
39	2.81
40	3.96
41	2.82
42	4.27
43	3.71
44	2.99
45	3.45
46	3.52
47	3.62
48	3.03

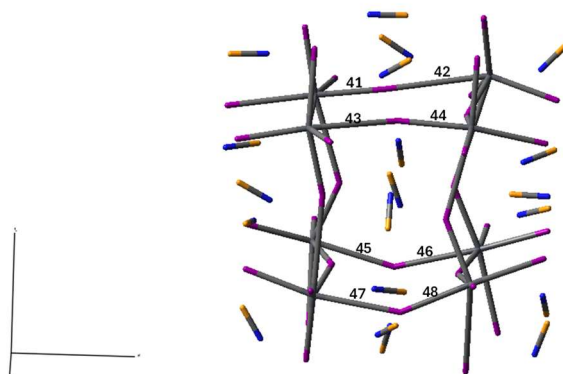
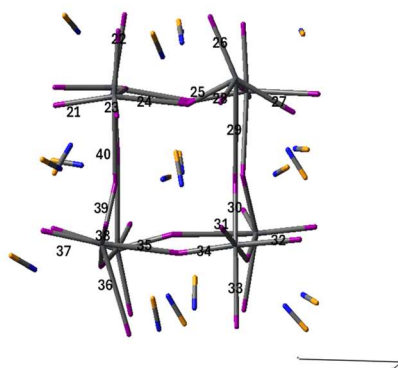
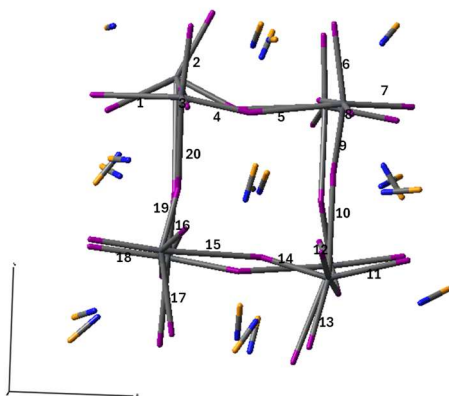


Table SII. Pb-I distances (d_{Pb-I}) for cluster 2-1-1 optimized using the GFN2-xTB method. For bond labels, refer to figure to the right.

Label	d_{Pb-I} (Å)	d_{Pb-I} (Å)
1	2.91	2.91
2	3.21	3.21
3	3.72	2.85
4	2.93	2.93
5	3.36	3.57
6	3.15	3.15
7	2.94	2.94
8	2.99	3.57
9	2.92	2.92
10	2.93	2.93
11	3.98	2.84
12	3.57	3.57
13	3.64	2.82
14	2.94	2.94
15	3.4	3.4
16	3.14	3.14
17	2.93	2.93
18	2.96	3.66
19	2.96	2.96
20	2.76	3.83
21	3.25	3.25
22	2.92	2.92
23	2.96	4.97
24	3.32	3.32
25	2.92	2.92
26	2.93	3.69
27	3.99	3.99
28	2.83	4.28
29	3.23	3.23
30	2.9	2.9
31	2.93	2.93
32	3.63	2.83
33	3.23	
34	3.15	
35	2.99	3.57
36	2.93	
37	2.96	
38	3.6	2.81
39	3.99	
40	2.93	
41	3.72	2.83
42	2.91	
43	3.25	
44	2.95	4.97
45	2.91	
46	3.21	
47	2.88	3.74
48	2.93	

Table SIII. Pb-I distances (d_{Pb-I}) for the central region of cluster 3-3-3 optimized using the GFN2-xTB method. For bond labels, refer to figure to the right.

Label	d_{Pb-I} (Å)
1	2.88
2	2.8
3	3.64
4	3.56
5	2.82
6	2.89
7	3.38
8	3.62
9	3.56
10	2.82
11	3.5
12	3.64
13	3.48
14	2.86
15	3.39
16	3.69
17	3.58
18	2.87
19	2.83
20	3.62
21	2.93
22	2.81
23	2.79
24	3.39
25	2.88
26	2.82
27	3.43
28	2.83
29	3.69
30	2.82
31	2.89
32	2.89
33	3.62
34	2.83
35	3.56
36	3.64
37	2.89
38	2.8
39	2.8
40	3.73
41	3.56
42	2.83
43	3.4
44	2.87
45	3.4
46	2.88
47	3.51
48	2.85

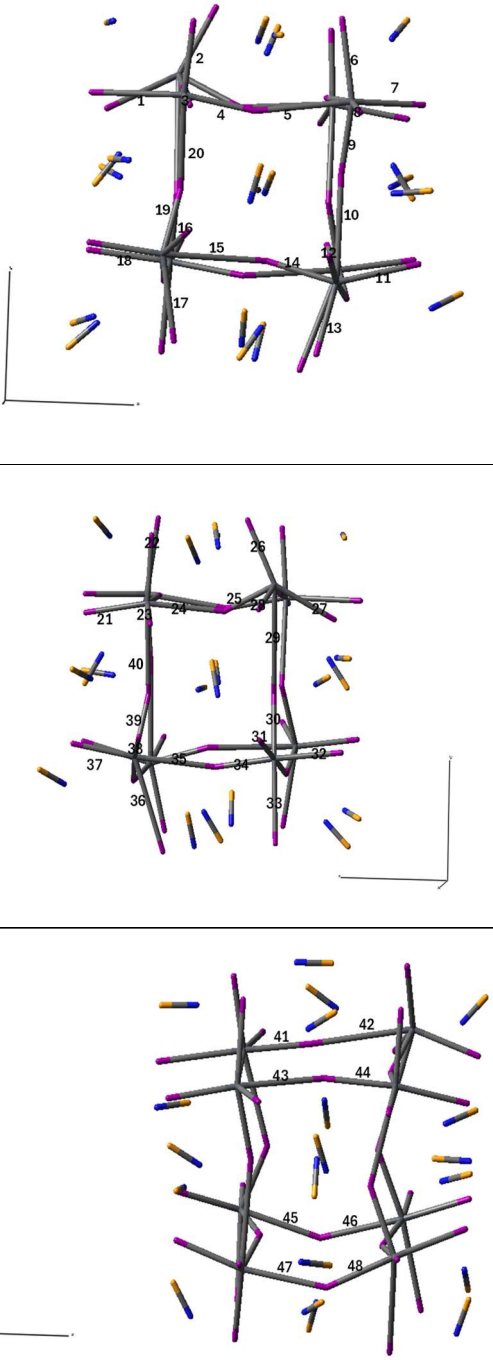


Table SIV. Pb-I distances (d_{Pb-I}) for the central region of cluster 4-3-3 optimized using the GFN2-xTB method. For bond labels, refer to figure to the right.

Label	d_{Pb-I} (Å)	d_{Pb-I} (Å)
1	3.50	
2	2.85	
3	2.84	3.58
4	3.69	
5	2.81	3.67
6	3.67	
7	2.87	
8	2.80	3.75
9	2.79	
10	2.85	
11	3.67	2.80
12	2.82	
13	3.51	2.81
14	3.86	
15	3.60	
16	2.82	3.62
17	2.88	
18	3.75	
19	3.55	2.83
20	2.85	
21	3.51	2.84
22	2.84	
23	3.55	
24	3.64	2.79
25	3.29	
26	3.79	
27	2.91	3.50
28	3.69	
29	2.86	3.44
30	2.84	
31	2.90	
32	3.70	2.83
33	2.84	
34	3.62	2.84
35	3.45	
36	2.93	
37	3.34	2.92
38	3.47	
39	2.88	
40	3.67	2.83
41	3.68	
42	2.91	
43	3.34	2.92
44	3.30	
45	3.53	
46	2.88	3.53
47	2.84	
48	3.25	
49	2.92	3.55
50	2.81	

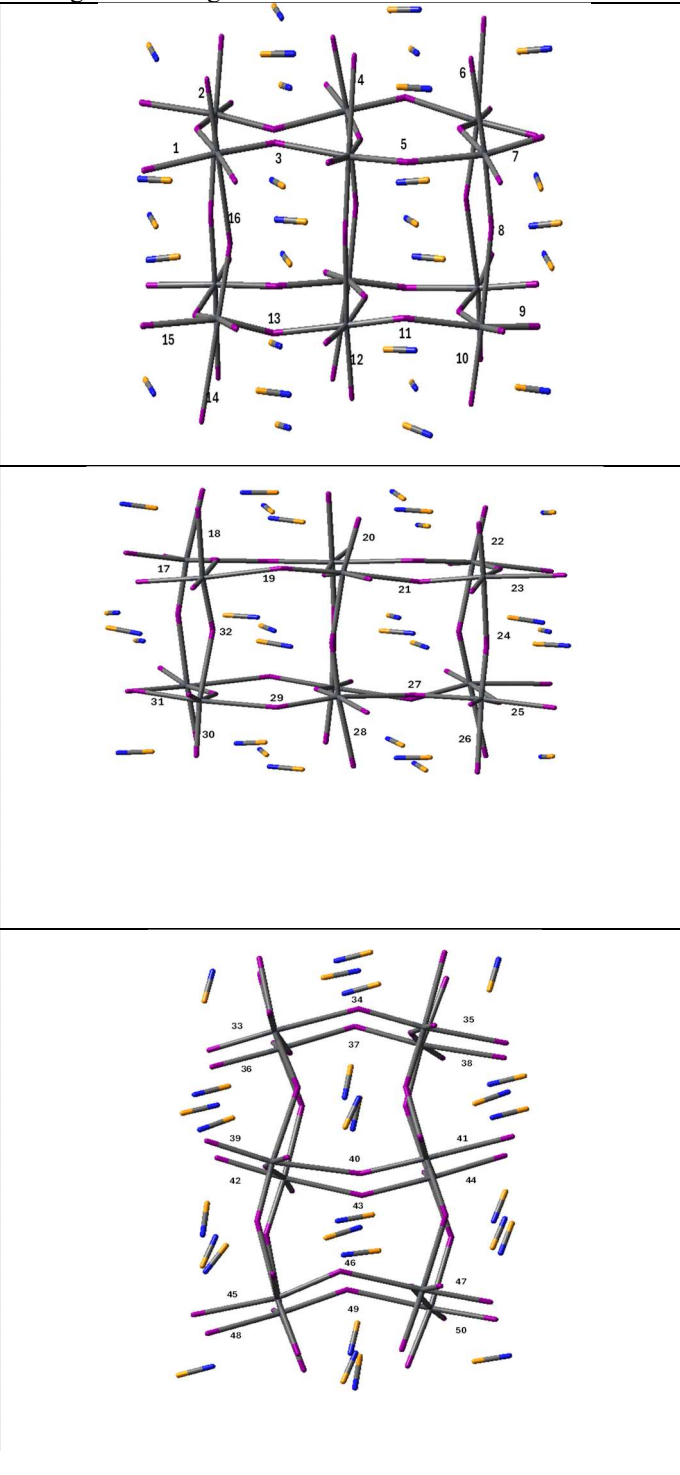


Table SV. Pb-I distances (d_{Pb-I}) for the central region of cluster 4-4-4 optimized using the GFN2-xTB method. For bond labels, refer to Table S4.

Label	d_{Pb-I} (Å)	d_{Pb-I} (Å)	Label	d_{Pb-I} (Å)	d_{Pb-I} (Å)
1	3.42		62	3.47	2.81
2	2.87		63	3.67	2.83
3	2.84	3.48	64	2.85	3.61
4	3.62		65	3.59	
5	2.85	3.49	66	3.62	
6	3.66		67	2.87	
7	2.86		68	2.82	3.7
8	2.81	3.78	69	2.85	
9	2.85		70	3.41	
10	2.78		71	2.83	3.72
11	3.63	2.85	72	2.84	
12	2.82		73	3.57	
13	3.61	2.85	74	2.85	
14	3.76		75	3.72	2.91
15	3.46		76	3.73	2.82
16	2.86		77	2.81	3.57
17	3.67		78	3.48	
18	3.54	2.83	79	3.69	
19	3.59		80	2.86	
20	3.58	2.83	81	2.79	3.7
21	3.69		82	2.90	
22	3.62		83	3.32	
23	2.83	3.66	84	2.79	3.74
24	3.52		85	2.90	
25	2.83		86	3.52	
26	2.86	3.60	87	2.82	
27	2.80		88	3.32	
28	2.80	3.67	89	3.78	
29	2.82		90	2.85	
30	2.84				
31	2.90				
32	2.85	3.55			
33	2.83				
34	2.84				
35	3.68	2.85			
36	3.54				
37	3.35				
38	2.82	3.48			
39	2.90				
40	2.84				
41	3.57	2.82			
42	3.72				
43	3.35				
44	2.89	3.47			
45	2.85				
46	2.84				
47	3.56	2.84			
48	3.46				
49	3.70				
50	2.83				
51	3.45				
52	2.85				
53	3.77	2.83			
54	2.81				
55	2.85				
56	3.68				
57	3.72	2.82			
58	3.61				
59	2.92				
60	2.82				
61	3.69				

Table SVI. Molecular orbital energies for clusters 1-1-1, 2-1-1, 3-3-3, 4-3-3 and 4-4-4. Units are in eV

	PBE0-D4/Def2-TZVP		ONIOM PBE0-D4/Def2-TZVP:GFN2- <i>xTB</i>		
	1-1-1	2-1-1	3-3-3	4-3-3	4-4-4
HOMO-9	-6.30	-6.09	-2.28	-2.02	-1.81
HOMO-8	-6.23	-5.98	-2.21	-1.95	-1.78
HOMO-7	-6.14	-5.94	-2.03	-1.89	-1.70
HOMO-6	-6.12	-5.88	-1.94	-1.81	-1.68
HOMO-5	-6.09	-5.83	-1.89	-1.81	-1.64
HOMO-4	-6.00	-5.80	-1.77	-1.60	-1.60
HOMO-3	-5.85	-5.72	-1.74	-1.56	-1.57
HOMO-2	-5.65	-5.65	-1.65	-1.45	-1.52
HOMO-1	-5.57	-5.60	-1.48	-1.41	-1.39
HOMO	-5.37	-5.51	-1.35	-1.13	-1.23
LUMO	-1.56	-1.44	0.46	0.86	0.49
LUMO+1	-1.41	-1.39	0.51	0.97	0.68
LUMO+2	-1.17	-1.35	0.63	1.16	0.77
LUMO+3	-1.13	-1.25	0.74	1.33	0.96
LUMO+4	-1.05	-1.20	0.99	1.36	1.00
LUMO+5	-0.96	-1.05	1.02	1.45	1.17
LUMO+6	-0.90	-0.99	1.17	1.52	1.19
LUMO+7	-0.87	-0.97	1.23	1.63	1.27
LUMO+8	-0.86	-0.96	1.35	1.67	1.28
LUMO+9	-0.60	-0.93	1.49	1.71	1.41
ΔE_{gap}^a	3.81	4.07	1.81	1.99	1.72

^a ΔE_{gap} defined as the energy difference between HOMO and LUMO orbitals.

Table SVII. Calculated vertical excitations energies (ΔE_{TD}), oscillator strengths (f) and main configurations for cluster 1-1-1 using TD-PBE0-D4/Def2-TZVP for the first 50 excited states.

	ΔE_{TD} (eV)	f	Configuration ^a		ΔE_{TD} (eV)	f	Configuration ^a
1	3.37	0.0496	HOMO-2 → LUMO (75%) HOMO-1 → LUMO (9%) HOMO → LUMO (5%)	26	4.11	0.0239	HOMO-6 → LUMO+1 (5%) HOMO-3 → LUMO+5 (5%) HOMO-1 → LUMO+4 (10%) HOMO-1 → LUMO+8 (7%) HOMO → LUMO+6 (12%) HOMO → LUMO+7 (8%) HOMO → LUMO+8 (8%)
2	3.46	0.0004	HOMO-2 → LUMO (6%) HOMO → LUMO (89%)	27	4.11	0.0243	HOMO-8 → LUMO (5%) HOMO-7 → LUMO+1 (5%) HOMO-6 → LUMO+1 (8%) HOMO-1 → LUMO+4 (15%) HOMO-1 → LUMO+7 (7%) HOMO-1 → LUMO+8 (5%) HOMO → LUMO+9 (10%)
3	3.55	0.0053	HOMO-1 → LUMO (7%) HOMO → LUMO+1 (87%)	28	4.11	0.0175	HOMO-19 → LUMO (5%) HOMO-11 → LUMO (21%) HOMO-9 → LUMO (13%) HOMO-6 → LUMO (8%)
4	3.58	0.0011	HOMO-2 → LUMO (6%) HOMO-1 → LUMO (78%) HOMO → LUMO+1 (8%)	29	4.12	0.0484	HOMO-8 → LUMO (20%) HOMO-7 → LUMO (6%) HOMO-6 → LUMO (7%) HOMO-5 → LUMO (9%) HOMO-3 → LUMO+5 (15%) HOMO-1 → LUMO+5 (7%)
5	3.72	0.0292	HOMO → LUMO+2 (45%) HOMO → LUMO+3 (11%) HOMO → LUMO+4 (25%) HOMO → LUMO+7 (5%)	30	4.13	0.0241	HOMO-3 → LUMO+5 (7%) HOMO-2 → LUMO+2 (13%) HOMO-2 → LUMO+6 (9%) HOMO-2 → LUMO+8 (9%) HOMO → LUMO+6 (8%) HOMO → LUMO+8 (14%)
6	3.75	0.0735	HOMO-6 → LUMO (7%) HOMO-4 → LUMO (55%) HOMO-3 → LUMO (7%) HOMO-2 → LUMO+1 (5%)	31	4.14	0.1782	HOMO-7 → LUMO (8%) HOMO-7 → LUMO+1 (7%) HOMO-6 → LUMO+1 (11%) HOMO-3 → LUMO+5 (9%) HOMO-1 → LUMO+5 (32%)
7	3.79	0.0141	HOMO-4 → LUMO+1 (5%) HOMO-2 → LUMO+1 (30%) HOMO-1 → LUMO+1 (45%)	32	4.15	0.0006	HOMO-3 → LUMO+5 (18%) HOMO-1 → LUMO+4 (13%) HOMO-1 → LUMO+5 (14%) HOMO-1 → LUMO+9 (6%) HOMO → LUMO+8 (13%) HOMO → LUMO+9 (10%)
8	3.82	0.0646	HOMO-4 → LUMO+1 (21%) HOMO-2 → LUMO+1 (9%) HOMO-1 → LUMO+1 (24%) HOMO → LUMO+2 (12%)	33	4.18	0.0541	HOMO-8 → LUMO+1 (5%) HOMO-4 → LUMO+2 (5%) HOMO-3 → LUMO+5 (9%) HOMO-1 → LUMO+5 (24%) HOMO → LUMO+8 (7%) HOMO → LUMO+9 (23%)
9	3.83	0.0181	HOMO-1 → LUMO+1 (15%) HOMO → LUMO+2 (32%) HOMO → LUMO+3 (19%) HOMO → LUMO+6 (5%)	34	4.19	0.1345	HOMO-8 → LUMO+1 (22%) HOMO-7 → LUMO+1 (5%) HOMO-4 → LUMO+1 (7%) HOMO-4 → LUMO+2 (13%) HOMO-3 → LUMO+5 (7%) HOMO → LUMO+9 (8%)
10	3.84	0.0347	HOMO-6 → LUMO+1 (5%) HOMO-4 → LUMO+1 (22%) HOMO-3 → LUMO (6%) HOMO-2 → LUMO+1 (42%) HOMO-1 → LUMO+1 (7%)	35	4.21	0.0257	HOMO-8 → LUMO+1 (15%) HOMO-6 → LUMO+1 (11%) HOMO-4 → LUMO (7%) HOMO-4 → LUMO+2 (29%)
11	3.86	0.0218	HOMO-2 → LUMO+3 (7%) HOMO → LUMO+3 (36%) HOMO → LUMO+5 (6%) HOMO → LUMO+6 (7%) HOMO → LUMO+7 (11%)	36	4.21	0.0192	HOMO-9 → LUMO (10%) HOMO-8 → LUMO+1 (7%) HOMO-4 → LUMO+3 (8%) HOMO-3 → LUMO+3 (11%) HOMO-3 → LUMO+4 (15%)
12	3.88	0.0297	HOMO-3 → LUMO (7%) HOMO-2 → LUMO+2 (7%) HOMO-2 → LUMO+3 (26%) HOMO-2 → LUMO+6 (8%) HOMO-2 → LUMO+8 (9%) HOMO → LUMO+3 (17%)	37	4.22	0.0053	HOMO-2 → LUMO+2 (7%) HOMO-2 → LUMO+3 (11%) HOMO-2 → LUMO+4 (54%)
13	3.88	0.0105	HOMO-7 → LUMO (8%) HOMO-4 → LUMO (7%)	38	4.23	0.0241	HOMO-9 → LUMO (10%) HOMO-5 → LUMO (41%)

			HOMO-4 → LUMO+1 (5%) HOMO-3 → LUMO (58%)				HOMO-1 → LUMO+7 (14%)
14	3.94	0.0070	HOMO-1 → LUMO+2 (6%) HOMO-1 → LUMO+3 (13%) HOMO → LUMO+4 (35%) HOMO → LUMO+5 (21%)	39	4.23	0.0449	HOMO-5 → LUMO (18%) HOMO-2 → LUMO+4 (8%) HOMO-1 → LUMO+7 (24%) HOMO-1 → LUMO+9 (6%) HOMO → LUMO+9 (6%)
15	3.94	0.0500	HOMO-3 → LUMO+1 (42%) HOMO-3 → LUMO+2 (14%) HOMO-3 → LUMO+3 (6%) HOMO-3 → LUMO+4 (6%) HOMO → LUMO+5 (7%)	40	4.26	0.0054	HOMO-9 → LUMO (8%) HOMO-3 → LUMO+2 (5%) HOMO-3 → LUMO+3 (5%) HOMO-1 → LUMO+6 (17%) HOMO-1 → LUMO+8 (26%)
16	3.96	0.0052	HOMO-3 → LUMO+1 (6%) HOMO-1 → LUMO+2 (5%) HOMO-1 → LUMO+3 (10%) HOMO → LUMO+5 (46%) HOMO → LUMO+6 (9%) HOMO → LUMO+7 (7%)	41	4.26	0.0023	HOMO-11 → LUMO (7%) HOMO-9 → LUMO (15%) HOMO-5 → LUMO (5%) HOMO-1 → LUMO+6 (6%) HOMO-1 → LUMO+8 (11%) HOMO → LUMO+10 (5%)
17	3.99	0.0217	HOMO-1 → LUMO+2 (12%) HOMO-1 → LUMO+3 (20%) HOMO → LUMO+4 (20%) HOMO → LUMO+6 (14%)	42	4.27	0.0604	HOMO → LUMO+10 (67%)
18	4.01	0.0169	HOMO-3 → LUMO+1 (7%) HOMO-2 → LUMO+2 (24%) HOMO-2 → LUMO+3 (20%) HOMO-2 → LUMO+4 (17%) HOMO-1 → LUMO+3 (7%)	43	4.28	0.0131	HOMO-7 → LUMO+1 (8%) HOMO-7 → LUMO+3 (5%) HOMO-4 → LUMO+3 (12%) HOMO-4 → LUMO+4 (5%) HOMO-3 → LUMO+2 (14%) HOMO-3 → LUMO+4 (8%) HOMO-1 → LUMO+8 (7%)
19	4.02	0.0025	HOMO-7 → LUMO (18%) HOMO-6 → LUMO (28%) HOMO-4 → LUMO (14%) HOMO-4 → LUMO+1 (5%)	44	4.30	0.0023	HOMO-8 → LUMO (5%) HOMO-4 → LUMO+3 (9%) HOMO-3 → LUMO+2 (10%) HOMO-3 → LUMO+3 (23%)
20	4.02	0.0463	HOMO-1 → LUMO+2 (21%) HOMO-1 → LUMO+4 (12%) HOMO-1 → LUMO+6 (9%) HOMO-1 → LUMO+8 (7%) HOMO → LUMO+7 (13%)	45	4.30	0.0093	HOMO-17 → LUMO (8%) HOMO-16 → LUMO (7%) HOMO-11 → LUMO (8%) HOMO-9 → LUMO (10%) HOMO-8 → LUMO (7%) HOMO-3 → LUMO+3 (10%)
21	4.03	0.0889	HOMO-3 → LUMO+1 (8%) HOMO-3 → LUMO+2 (5%) HOMO-1 → LUMO+2 (12%) HOMO-1 → LUMO+3 (16%) HOMO-1 → LUMO+6 (11%) HOMO → LUMO+7 (10%)	46	4.31	0.0181	HOMO-7 → LUMO+1 (11%) HOMO-3 → LUMO+6 (6%) HOMO-3 → LUMO+7 (8%) HOMO-3 → LUMO+8 (9%) HOMO-2 → LUMO+5 (7%) HOMO-2 → LUMO+7 (10%) HOMO-1 → LUMO+7 (7%)
22	4.05	0.0289	HOMO-3 → LUMO+1 (12%) HOMO-3 → LUMO+2 (16%) HOMO-3 → LUMO+4 (13%) HOMO-1 → LUMO+2 (28%)	47	4.32	0.0025	HOMO-2 → LUMO+5 (26%) HOMO-2 → LUMO+6 (22%) HOMO-2 → LUMO+7 (16%) HOMO-2 → LUMO+8 (11%)
23	4.08	0.0284	HOMO-8 → LUMO (16%) HOMO-7 → LUMO (20%) HOMO-4 → LUMO+2 (9%) HOMO-1 → LUMO+8 (5%)	48	4.32	0.0214	HOMO-7 → LUMO+1 (17%) HOMO-5 → LUMO+1 (24%) HOMO-3 → LUMO+4 (9%)
24	4.09	0.0330	HOMO-1 → LUMO+4 (29%) HOMO-1 → LUMO+6 (8%) HOMO → LUMO+7 (19%) HOMO → LUMO+8 (12%)	49	4.34	0.0046	HOMO-8 → LUMO+1 (9%) HOMO-7 → LUMO+1 (6%) HOMO-6 → LUMO+1 (17%) HOMO-5 → LUMO+1 (46%)
25	4.09	0.0090	HOMO-2 → LUMO+2 (15%) HOMO-2 → LUMO+6 (7%) HOMO-2 → LUMO+8 (7%) HOMO → LUMO+6 (8%) HOMO → LUMO+8 (14%)	50	4.36	0.0410	HOMO-6 → LUMO+2 (13%) HOMO-4 → LUMO+3 (10%) HOMO-4 → LUMO+4 (23%) HOMO-2 → LUMO+5 (13%)

^a Percentage contribution in parentheses

Table SVIII. Calculated vertical excitations energies (ΔE_{TD}), oscillator strengths (f) and main configurations for cluster 2-1-1 using TD-PBE0-D4/Def2-TZVP for the first 50 excited states.

	ΔE_{TD} (eV)	f	Configuration ^a		ΔE_{TD} (eV)	f	Configuration ^a
1	3.49	0.0434	HOMO-2 → LUMO (73%) HOMO → LUMO (6%)	26	26	4.01	HOMO-7 → LUMO+1 (5%) HOMO-5 → LUMO (7%) HOMO-5 → LUMO+2 (7%) HOMO-3 → LUMO+3 (26%) HOMO → LUMO+3 (6%)
2	3.61	0.0247	HOMO-2 → LUMO (5%) HOMO → LUMO (83%)	27	27	4.02	HOMO-8 → LUMO+1 (8%) HOMO-7 → LUMO+1 (5%) HOMO-7 → LUMO+2 (14%) HOMO-6 → LUMO+2 (6%)
3	3.65	0.0512	HOMO-3 → LUMO+1 (9%) HOMO-1 → LUMO (11%) HOMO-1 → LUMO+1 (22%) HOMO-1 → LUMO+2 (24%)	28	28	4.02	HOMO-3 → LUMO+4 (14%) HOMO-2 → LUMO+1 (26%) HOMO-2 → LUMO+2 (9%)
4	3.68	0.1229	HOMO-6 → LUMO+1 (16%) HOMO-5 → LUMO+1 (8%) HOMO-3 → LUMO+1 (18%) HOMO-3 → LUMO+2 (9%) HOMO-1 → LUMO+2 (16%)	29	29	4.04	HOMO-8 → LUMO+2 (6%) HOMO-5 → LUMO (1%) HOMO-5 → LUMO+2 (12%) HOMO-1 → LUMO+6 (5%)
5	3.72	0.0265	HOMO-3 → LUMO+1 (6%) HOMO-1 → LUMO (5%) HOMO-1 → LUMO+1 (38%) HOMO-1 → LUMO+2 (7%) HOMO-1 → LUMO+4 (11%) HOMO → LUMO+1 (9%)	30	30	4.04	HOMO-7 → LUMO+1 (6%) HOMO-6 → LUMO (8%) HOMO-6 → LUMO+2 (5%) HOMO-6 → LUMO+4 (7%) HOMO-5 → LUMO+2 (9%) HOMO-5 → LUMO+3 (6%) HOMO-3 → LUMO+3 (6%)
6	3.74	0.0687	HOMO-3 → LUMO+2 (7%) HOMO-1 → LUMO (12%) HOMO-1 → LUMO+1 (5%) HOMO-1 → LUMO+2 (9%) HOMO-1 → LUMO+3 (9%) HOMO → LUMO+1 (11%) HOMO → LUMO+2 (21%)	31	31	4.05	HOMO-5 → LUMO+2 (5%) HOMO-4 → LUMO+4 (9%) HOMO-3 → LUMO+4 (5%) HOMO-1 → LUMO+21 (6%)
7	3.75	0.0174	HOMO-1 → LUMO (54%) HOMO-1 → LUMO+1 (9%) HOMO-1 → LUMO+2 (13%) HOMO → LUMO+2 (5%)	32	32	4.05	HOMO-7 → LUMO+2 (5%) HOMO-5 → LUMO (8%) HOMO-1 → LUMO+7 (9%) HOMO-1 → LUMO+8 (7%)
8	3.78	0.1481	HOMO-6 → LUMO+1 (7%) HOMO-5 → LUMO+1 (6%) HOMO → LUMO+1 (39%) HOMO → LUMO+2 (15%)	33	33	4.06	HOMO0 → LUMO+1 (7%) HOMO-8 → LUMO+2 (6%) HOMO-2 → LUMO+3 (6%)
9	3.80	0.0289	HOMO-8 → LUMO (5%) HOMO-7 → LUMO (5%) HOMO-4 → LUMO (10%) HOMO-3 → LUMO (18%) HOMO → LUMO+2 (10%) HOMO → LUMO+4 (6%)	34	34	4.06	HOMO-6 → LUMO+2 (10%) HOMO-3 → LUMO+4 (5%) HOMO-1 → LUMO+6 (6%)
10	3.83	0.0279	HOMO-4 → LUMO (12%) HOMO-3 → LUMO+1 (6%) HOMO-3 → LUMO+2 (8%) HOMO-1 → LUMO+3 (7%) HOMO-1 → LUMO+4 (6%) HOMO → LUMO+1 (5%) HOMO → LUMO+2 (10%) HOMO → LUMO+4 (8%) HOMO → LUMO+5 (6%)	35	35	4.08	HOMO-9 → LUMO+1 (6%) HOMO-8 → LUMO+2 (5%) HOMO-7 → LUMO+1 (8%) HOMO-5 → LUMO+4 (5%) HOMO-1 → LUMO+5 (13%) HOMO-1 → LUMO+6 (9%)
11	3.83	0.1600	HOMO-1 → LUMO+2 (7%) HOMO-1 → LUMO+3 (21%) HOMO-1 → LUMO+4 (18%) HOMO → LUMO+1 (8%) HOMO → LUMO+2 (7%)	36	36	4.08	HOMO-8 → LUMO+2 (5%) HOMO-7 → LUMO+2 (8%) HOMO-1 → LUMO+8 (10%) HOMO-1 → LUMO+9 (8%)
12	3.84	0.0431	HOMO-3 → LUMO+1 (9%) HOMO-3 → LUMO+2 (8%) HOMO → LUMO+3 (15%) HOMO → LUMO+4 (13%)	37	37	4.09	HOMO-3 → LUMO+4 (7%) HOMO-2 → LUMO+3 (18%) HOMO-2 → LUMO+5 (11%) HOMO → LUMO+10 (5%)
13	3.86	0.0074	HOMO-3 → LUMO+3 (5%) HOMO-2 → LUMO+1 (5%) HOMO-2 → LUMO+2 (11%) HOMO-2 → LUMO+3 (12%) HOMO-2 → LUMO+5 (20%)	38	38	4.09	HOMO-4 → LUMO+1 (32%) HOMO-4 → LUMO+2 (24%) HOMO-2 → LUMO+4 (6%)
14	3.88	0.0362	HOMO-4 → LUMO (17%) HOMO-3 → LUMO+2 (6%)	39	39	4.10	HOMO-1 → LUMO+5 (9%) HOMO-1 → LUMO+6 (11%)

			HOMO-2 → LUMO+3 (6%) HOMO-1 → LUMO+3 (10%) HOMO → LUMO+4 (17%)				HOMO → LUMO+10 (9%)
15	3.88	0.0048	HOMO-8 → LUMO (12%) HOMO-7 → LUMO (8%) HOMO-4 → LUMO (7%) HOMO-2 → LUMO+2 (12%) HOMO → LUMO+3 (20%)	40	40	4.11	HOMO-2 → LUMO+4 (15%) HOMO → LUMO+6 (7%) HOMO → LUMO+9 (15%)
16	3.89	0.0099	HOMO-7 → LUMO (5%) HOMO-3 → LUMO+2 (9%) HOMO-2 → LUMO+1 (10%) HOMO-2 → LUMO+2 (32%) HOMO-2 → LUMO+3 (10%)	41	41	4.11	HOMO-4 → LUMO+2 (13%) HOMO-2 → LUMO+4 (15%)
17	3.90	0.0062	HOMO-4 → LUMO (7%) HOMO-3 → LUMO+1 (5%) HOMO-3 → LUMO+2 (12%) HOMO-1 → LUMO+4 (11%) HOMO → LUMO+4 (6%) HOMO → LUMO+5 (10%)	42	42	4.12	HOMO-4 → LUMO+2 (16%) HOMO-2 → LUMO+4 (6%) HOMO → LUMO+5 (13%) HOMO → LUMO+6 (6%)
18	3.91	0.0254	HOMO-7 → LUMO (5%) HOMO-6 → LUMO+1 (5%) HOMO-3 → LUMO+1 (6%) HOMO-1 → LUMO+3 (7%) HOMO-1 → LUMO+4 (10%) HOMO → LUMO+3 (27%)	43	43	4.12	HOMO-5 → LUMO+3 (11%) HOMO-5 → LUMO+4 (10%) HOMO-1 → LUMO+5 (10%) HOMO → LUMO+10 (6%)
19	3.93	0.0455	HOMO-8 → LUMO (11%) HOMO-7 → LUMO+1 (6%) HOMO-7 → LUMO+2 (7%) HOMO-3 → LUMO (5%) HOMO-3 → LUMO+3 (5%) HOMO → LUMO+3 (9%) HOMO → LUMO+5 (6%)	44	44	4.13	HOMO-1 → LUMO+5 (28%) HOMO-1 → LUMO+7 (7%) HOMO → LUMO+9 (5%)
20	3.94	0.0158	HOMO-7 → LUMO (10%) HOMO-3 → LUMO (22%) HOMO-1 → LUMO+3 (8%)	45	45	4.14	HOMO7 → LUMO (5%) HOMO1 → LUMO (46%) HOMO-9 → LUMO (21%)
21	3.95	0.0054	HOMO-6 → LUMO+1 (11%) HOMO-5 → LUMO+1 (23%) HOMO-5 → LUMO+4 (7%)	46	46	4.14	HOMO-6 → LUMO+2 (8%) HOMO-5 → LUMO+3 (11%) HOMO-4 → LUMO+3 (6%) HOMO → LUMO+5 (8%) HOMO → LUMO+7 (7%) HOMO → LUMO+8 (6%) HOMO → LUMO+21 (5%)
22	3.96	0.0499	HOMO-3 → LUMO (15%) HOMO-3 → LUMO+2 (5%) HOMO → LUMO+1 (5%) HOMO → LUMO+5 (14%)	47	47	4.15	HOMO-5 → LUMO+3 (13%) HOMO-5 → LUMO+4 (9%) HOMO-2 → LUMO+5 (5%)
23	3.97	0.0298	HOMO-5 → LUMO (14%) HOMO-5 → LUMO+2 (18%) HOMO-1 → LUMO+9 (5%) HOMO-1 → LUMO+10 (5%)	48	48	4.17	HOMO → LUMO+6 (6%) HOMO → LUMO+7 (11%) HOMO → LUMO+8 (14%)
24	3.98	0.0004	HOMO-4 → LUMO (5%) HOMO-3 → LUMO+4 (6%) HOMO-2 → LUMO+1 (17%) HOMO-2 → LUMO+2 (9%) HOMO-2 → LUMO+4 (11%)	49	49	4.17	HOMO-8 → LUMO+2 (10%) HOMO-7 → LUMO+3 (17%) HOMO-6 → LUMO (14%) HOMO-6 → LUMO+3 (6%)
25	4.00	0.0824	HOMO-5 → LUMO (10%) HOMO-1 → LUMO+7 (6%) HOMO-1 → LUMO+9 (8%) HOMO-1 → LUMO+21 (6%)	50	50	4.18	HOMO-8 → LUMO+2 (10%) HOMO-7 → LUMO+3 (6%) HOMO-6 → LUMO (13%) HOMO-6 → LUMO+2 (6%) HOMO-4 → LUMO+1 (9%) HOMO-4 → LUMO+4 (5%)

^a Percentage contribution in parentheses.

Table SIX. Calculated vertical excitations energies (ΔE_{TD}), oscillator strengths (f) and main configurations for cluster 3-3-3 using TD-PBE0-D4/Def2-TZVP:GFN2-xTB for the first 50 excited states.

	ΔE_{TD} (eV)	f	Configuration ^a		ΔE_{TD} (eV)	f	Configuration ^a
1	1.50	0.0160	HOMO \rightarrow LUMO (97%)	26	2.17	0.0006	HOMO-6 \rightarrow LUMO+1 (94%)
2	1.55	0.1048	HOMO \rightarrow LUMO+1 (96%)	27	2.19	0.0460	HOMO-3 \rightarrow LUMO+3 (97%)
3	1.64	0.0031	HOMO-1 \rightarrow LUMO (96%)	28	2.21	0.0973	HOMO-7 \rightarrow LUMO (68%) HOMO-1 \rightarrow LUMO+5 (24%)
4	1.69	0.0007	HOMO-1 \rightarrow LUMO+1 (87%) HOMO \rightarrow LUMO+2 (7%)	29	2.21	0.1818	HOMO-7 \rightarrow LUMO (29%) HOMO-1 \rightarrow LUMO+4 (6%) HOMO-1 \rightarrow LUMO+5 (58%)
5	1.70	0.1504	HOMO-1 \rightarrow LUMO+1 (8%) HOMO \rightarrow LUMO+2 (88%)	30	2.22	0.0475	HOMO-4 \rightarrow LUMO+3 (96%)
6	1.77	0.0349	HOMO \rightarrow LUMO+3 (98%)	31	2.24	0.6004	HOMO \rightarrow LUMO+7 (87%) HOMO \rightarrow LUMO+8 (5%)
7	1.84	0.0450	HOMO-1 \rightarrow LUMO+2 (93%)	32	2.26	0.0329	HOMO-7 \rightarrow LUMO+1 (94%)
8	1.84	0.0023	HOMO-2 \rightarrow LUMO (94%)	33	2.27	0.0182	HOMO-1 \rightarrow LUMO+6 (94%)
9	1.90	0.0112	HOMO-2 \rightarrow LUMO+1 (89%)	34	2.28	0.0039	HOMO-5 \rightarrow LUMO+2 (95%)
10	1.91	0.0030	HOMO-3 \rightarrow LUMO (90%)	35	2.31	0.0576	HOMO-3 \rightarrow LUMO+4 (15%) HOMO-2 \rightarrow LUMO+4 (72%) HOMO-2 \rightarrow LUMO+5 (5%)
11	1.92	0.0478	HOMO-1 \rightarrow LUMO+3 (96%)	36	2.32	0.0125	HOMO-6 \rightarrow LUMO+2 (93%)
12	1.95	0.4351	HOMO-4 \rightarrow LUMO (60%) HOMO \rightarrow LUMO+4 (33%)	37	2.34	0.0131	HOMO-5 \rightarrow LUMO+3 (97%)
13	1.95	0.4611	HOMO-4 \rightarrow LUMO (37%) HOMO \rightarrow LUMO+4 (54%) HOMO \rightarrow LUMO+5 (6%)	38	2.38	0.2567	HOMO-9 \rightarrow LUMO (49%) HOMO-8 \rightarrow LUMO (23%) HOMO-3 \rightarrow LUMO+4 (14%) HOMO-2 \rightarrow LUMO+4 (5%)
14	1.97	0.0068	HOMO-3 \rightarrow LUMO+1 (92%)	39	2.38	0.0065	HOMO-9 \rightarrow LUMO (15%) HOMO-8 \rightarrow LUMO (6%) HOMO-3 \rightarrow LUMO+4 (49%) HOMO-2 \rightarrow LUMO+4 (16%)
15	2.01	0.0126	HOMO-4 \rightarrow LUMO+1 (96%)	40	2.38	0.3425	HOMO-1 \rightarrow LUMO+7 (80%) HOMO \rightarrow LUMO+8 (8%)
16	2.04	0.0005	HOMO-2 \rightarrow LUMO+2 (93%)	41	2.38	0.0480	HOMO-1 \rightarrow LUMO+7 (5%) HOMO \rightarrow LUMO+7 (6%) HOMO \rightarrow LUMO+8 (81%)
17	2.06	0.3149	HOMO \rightarrow LUMO+4 (9%) HOMO \rightarrow LUMO+5 (84%)	42	2.39	0.0372	HOMO-6 \rightarrow LUMO+3 (95%)
18	2.07	0.0025	HOMO-5 \rightarrow LUMO (98%)	43	2.39	0.0672	HOMO-3 \rightarrow LUMO+4 (5%) HOMO-2 \rightarrow LUMO+5 (87%)
19	2.08	0.0651	HOMO-1 \rightarrow LUMO+4 (86%) HOMO-1 \rightarrow LUMO+5 (11%)	44	2.40	0.0247	HOMO-9 \rightarrow LUMO (28%) HOMO-8 \rightarrow LUMO (66%)
20	2.11	0.0018	HOMO-3 \rightarrow LUMO+2 (61%) HOMO-2 \rightarrow LUMO+3 (32%)	45	2.41	0.0167	HOMO-7 \rightarrow LUMO+2 (94%)
21	2.11	0.0926	HOMO-6 \rightarrow LUMO (65%) HOMO-3 \rightarrow LUMO+2 (17%) HOMO-2 \rightarrow LUMO+3 (14%)	46	2.42	1.0016	HOMO-9 \rightarrow LUMO+1 (76%) HOMO-8 \rightarrow LUMO+1 (14%)
22	2.11	0.0208	HOMO-6 \rightarrow LUMO (30%) HOMO-3 \rightarrow LUMO+2 (14%) HOMO-2 \rightarrow LUMO+3 (51%)	47	2.44	0.0775	HOMO-4 \rightarrow LUMO+4 (94%)
23	2.13	0.0107	HOMO-5 \rightarrow LUMO+1 (92%)	48	2.46	0.1034	HOMO-9 \rightarrow LUMO+1 (15%) HOMO-8 \rightarrow LUMO+1 (80%)
24	2.14	0.2707	HOMO \rightarrow LUMO+6 (95%)	49	2.47	0.5958	HOMO-4 \rightarrow LUMO+5 (27%) HOMO-3 \rightarrow LUMO+4 (5%) HOMO-3 \rightarrow LUMO+5 (57%)
25	2.16	0.0001	HOMO-4 \rightarrow LUMO+2 (95%)	50	2.47	0.6219	HOMO-10 \rightarrow LUMO (86%)

^a Percentage contribution in parentheses.

Table SX. Calculated vertical excitations energies (ΔE_{TD}), oscillator strengths (f) and main configurations for cluster 4-3-3 using TD-PBE0-D4/Def2-TZVP:GFN2-xTB for the first 50 excited states.

	ΔE_{TD} (eV)	f	Configuration ^a		ΔE_{TD} (eV)	f	Configuration ^a
1	1.74	0.0028	HOMO \rightarrow LUMO (99%)	26	2.52	0.0122	HOMO-1 \rightarrow LUMO+4 (93%)
2	1.86	0.0151	HOMO \rightarrow LUMO+1 (98%)	27	2.54	0.0305	HOMO \rightarrow LUMO+8 (34%) HOMO \rightarrow LUMO+9 (63%)
3	2.01	0.0274	HOMO \rightarrow LUMO+2 (98%)	28	2.55	0.0626	HOMO-2 \rightarrow LUMO+4 (90%)
4	2.03	0.0001	HOMO-1 \rightarrow LUMO (98%)	29	2.56	0.0032	HOMO-8 \rightarrow LUMO (89%)
5	2.06	0.0002	HOMO-2 \rightarrow LUMO (98%)	30	2.56	0.1834	HOMO-6 \rightarrow LUMO+1 (64%) HOMO-5 \rightarrow LUMO+1 (26%)
6	2.15	0.0094	HOMO-1 \rightarrow LUMO+1 (98%)	31	2.56	0.0016	HOMO \rightarrow LUMO+8 (63%) HOMO \rightarrow LUMO+9 (33%)
7	2.18	0.0001	HOMO-3 \rightarrow LUMO (98%)	32	2.57	0.0006	HOMO-6 \rightarrow LUMO+1 (28%) HOMO-5 \rightarrow LUMO+1 (70%)
8	2.18	0.0003	HOMO-2 \rightarrow LUMO+1 (97%)	33	2.60	0.2681	HOMO-1 \rightarrow LUMO+5 (35%) HOMO-1 \rightarrow LUMO+6 (59%)
9	2.18	0.1050	HOMO \rightarrow LUMO+3 (91%) HOMO \rightarrow LUMO+4 (6%)	34	2.63	0.0523	HOMO-7 \rightarrow LUMO+1 (84%) HOMO-3 \rightarrow LUMO+3 (9%)
10	2.22	0.0013	HOMO-4 \rightarrow LUMO (99%)	35	2.63	0.0367	HOMO-7 \rightarrow LUMO+1 (10%) HOMO-3 \rightarrow LUMO+3 (86%)
11	2.22	0.1737	HOMO \rightarrow LUMO+3 (5%) HOMO \rightarrow LUMO+4 (92%)	36	2.63	0.0595	HOMO-1 \rightarrow LUMO+5 (60%) HOMO-1 \rightarrow LUMO+6 (34%)
12	2.29	0.0149	HOMO-1 \rightarrow LUMO+2 (96%)	37	2.64	0.0406	HOMO-11 \rightarrow LUMO (6%) HOMO-9 \rightarrow LUMO (85%)
13	2.30	0.0001	HOMO-3 \rightarrow LUMO+1 (98%)	38	2.65	0.0192	HOMO \rightarrow LUMO+10 (95%)
14	2.32	0.5843	HOMO \rightarrow LUMO+5 (73%) HOMO \rightarrow LUMO+6 (23%)	39	2.65	0.1841	HOMO-2 \rightarrow LUMO+5 (37%) HOMO-2 \rightarrow LUMO+6 (57%)
15	2.33	0.0045	HOMO-2 \rightarrow LUMO+2 (93%)	40	2.66	0.0078	HOMO-11 \rightarrow LUMO (77%) HOMO-9 \rightarrow LUMO (8%) HOMO-4 \rightarrow LUMO+3 (5%)
16	2.34	0.0011	HOMO-4 \rightarrow LUMO+1 (95%)	41	2.66	0.0024	HOMO-4 \rightarrow LUMO+3 (90%)
17	2.34	0.9990	HOMO \rightarrow LUMO+5 (22%) HOMO \rightarrow LUMO+6 (72%)	42	2.67	0.0365	HOMO-3 \rightarrow LUMO+4 (96%)
18	2.43	0.0326	HOMO-6 \rightarrow LUMO (65%) HOMO-5 \rightarrow LUMO (32%)	43	2.67	0.0611	HOMO-2 \rightarrow LUMO+5 (58%) HOMO-2 \rightarrow LUMO+6 (37%)
19	2.43	0.0056	HOMO-6 \rightarrow LUMO (32%) HOMO-5 \rightarrow LUMO (66%)	44	2.68	0.0162	HOMO-8 \rightarrow LUMO+1 (91%)
20	2.46	0.0172	HOMO-3 \rightarrow LUMO+2 (98%)	45	2.69	0.0006	HOMO1 \rightarrow LUMO (94%)
21	2.47	0.0073	HOMO-1 \rightarrow LUMO+3 (94%)	46	2.70	0.0034	HOMO-6 \rightarrow LUMO+2 (17%) HOMO-5 \rightarrow LUMO+2 (76%)
22	2.49	0.0018	HOMO-4 \rightarrow LUMO+2 (98%)	47	2.70	0.0427	HOMO-4 \rightarrow LUMO+4 (95%)
23	2.50	0.0236	HOMO \rightarrow LUMO+6 (97%)	48	2.73	0.0031	HOMO-6 \rightarrow LUMO+2 (78%) HOMO-5 \rightarrow LUMO+2 (17%)
24	2.50	0.0023	HOMO-7 \rightarrow LUMO (93%)	49	2.77	0.1404	HOMO-11 \rightarrow LUMO+1 (15%) HOMO-9 \rightarrow LUMO+1 (59%) HOMO-7 \rightarrow LUMO+2 (11%)
25	2.51	0.0113	HOMO-2 \rightarrow LUMO+3 (91%)	50	2.77	0.0800	HOMO-9 \rightarrow LUMO+1 (18%) HOMO-7 \rightarrow LUMO+2 (71%)

^a Percentage contribution in parentheses.

Table SXI. Calculated vertical excitations energies (ΔE_{TD}), oscillator strengths (f) and main configurations for cluster 4-4-4 using TD-PBE0-D4/Def2-TZVP:GFN2-xTB for the first 10 excited states.

	ΔE_{TD} (eV)	f	Configuration ^a		ΔE_{TD} (eV)	f	Configuration ^a
1	1.50	0.0017	HOMO \rightarrow LUMO (99%)	6	1.85	0.0004	HOMO-3 \rightarrow LUMO (12%) HOMO-1 \rightarrow LUMO+1 (85%)
2	1.65	0.0012	HOMO-1 \rightarrow LUMO (99%)	7	1.85	0.0001	HOMO-3 \rightarrow LUMO (78%) HOMO-1 \rightarrow LUMO+1 (14%)
3	1.69	0.0017	HOMO \rightarrow LUMO+1 (99%)	8	1.89	0.0001	HOMO-4 \rightarrow LUMO (89%) HOMO-3 \rightarrow LUMO (7%)
4	1.76	0.0059	HOMO-2 \rightarrow LUMO (98%)	9	1.91	0.0066	HOMO-6 \rightarrow LUMO (22%) HOMO-5 \rightarrow LUMO (70%)
5	1.78	0.0006	HOMO \rightarrow LUMO+2 (99%)	10	1.94	0.0000	HOMO-6 \rightarrow LUMO (10%) HOMO-1 \rightarrow LUMO+2 (87%)

^a Percentage contribution in parentheses.

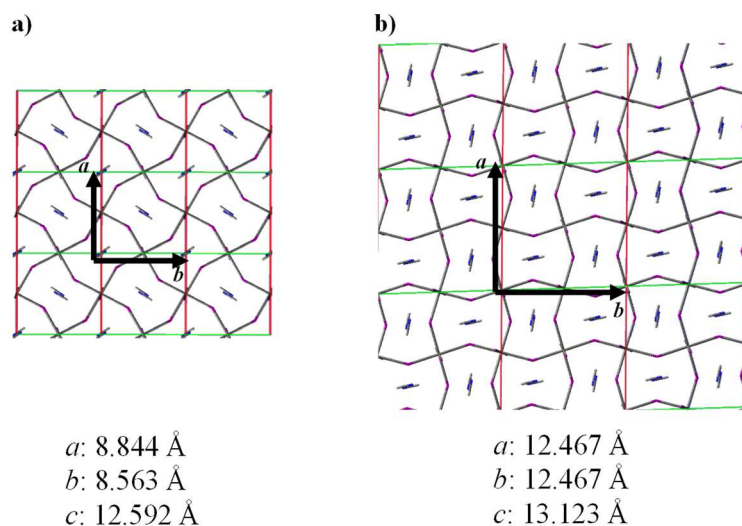


Figure S1. a) (*quasi*-)orthorhombic unit cell of the MAPI perovskite. Taken from Varadwaj *et al.*¹; b) (*quasi*-)cubic unit cell used in this work for the construction of cluster models.

References

- (1) Varadwaj, P. R.; Varadwaj, A.; Marques, H. M.; Yamashita, K. Significance of hydrogen bonding and other noncovalent interactions in determining octahedral tilting in the CH₃NH₃PbI₃ hybrid organic-inorganic halide perovskite solar cell semiconductor. *Sci. Rep* **2019**, *9*, 50. DOI: 10.1038/s41598-018-36218-1.