

Electronic Supplementary Information

Ligand effect on surface reconstructions in CdSe quantum dots driven by electron injection in electroluminescent processes

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Table S1 Bondlengths of (CdSe)₆ in this work and other studies.

Bondlengths (Å)		References
Facial	Interfacial	
2.596–2.597	2.818	This study
2.626	2.857	1
2.732 (average)		2
2.698–2.863		3

Table S2 Selected bondlengths (in Å) of (CdSe)₆-NH₂CH₃, (CdSe)₆-CdCl₂ and (CdSe)₆-SCH₃.

	D ₆₋₉	D ₆₋₁₁	D ₆₋₁₂	D ₆₋₂₉
(CdSe) ₆ -NH ₂ CH ₃	2.747	2.692	2.717	2.405
	D ₈₋₄	D ₈₋₂	D ₈₋₁	D ₈₋₇
(CdSe) ₆ -CdCl ₂	2.747	2.677	2.648	2.772
	D ₄₋₇	D ₄₋₁₀	D ₄₋₁₁	D ₄₋₂₇
(CdSe) ₆ -SCH ₃	2.742	2.840	2.844	2.447

Table S3 Amounts of atomic net charge and their changes (in e) of (CdSe)₆-NH₂CH₃ and (CdSe)₆-CdCl₂ before and after electron injection.

Atomic numbering	Element	(CdSe) ₆ -NH ₂ CH ₃			Element	(CdSe) ₆ -CdCl ₂		
		Before	After	Change		Before	After	Change
1	Cd	0.291	0.284	0.007	Cd	0.304	0.282	0.023
2	Cd	0.289	0.296	-0.007	Cd	0.306	0.273	0.033
3	Cd	0.288	0.290	-0.002	Cd	0.312	0.287	0.025
4	Cd	0.292	0.262	0.030	Cd	0.315	0.267	0.048
5	Cd	0.292	0.258	0.034	Cd	0.311	0.283	0.028
6	Cd	0.298	0.015	0.283	Cd	0.312	0.280	0.031
7	Se	-0.121	-0.115	-0.006	Cd	0.270	0.211	0.059
8	Se	-0.120	-0.132	0.012	Se	-0.226	-0.283	0.057
9	Se	-0.127	-0.239	0.112	Se	-0.101	-0.160	0.059
10	Se	-0.125	-0.143	0.018	Se	-0.102	-0.116	0.014
11	Se	-0.140	-0.129	-0.011	Se	-0.076	-0.147	0.071
12	Se	-0.135	-0.143	0.009	Se	-0.099	-0.127	0.027
13	H	-0.090	-0.123	0.033	Se	-0.105	-0.161	0.056
14	H	-0.101	-0.119	0.018	H	-0.099	-0.153	0.054
15	H	-0.096	-0.107	0.011	H	-0.101	-0.142	0.041
16	H	-0.089	-0.122	0.033	H	-0.098	-0.130	0.032
17	H	-0.094	-0.145	0.051	H	-0.099	-0.142	0.043
18	H	-0.102	-0.129	0.027	H	-0.096	-0.132	0.036
19	H	-0.118	-0.182	0.063	H	-0.100	-0.125	0.024
20	H	-0.116	-0.118	0.002	H	-0.077	-0.106	0.030
21	H	-0.116	-0.156	0.040	H	-0.072	-0.085	0.012
22	H	-0.119	-0.149	0.030	H	-0.074	-0.090	0.016
23	H	-0.117	-0.141	0.024	H	-0.076	-0.120	0.044
24	H	0.121	0.092	0.028	H	-0.075	-0.081	0.006
25	H	0.120	0.096	0.024	Cl	-0.235	-0.292	0.057
26	H	0.043	0.042	0.002	Cl	-0.219	-0.292	0.073
27	H	0.047	0.024	0.023				
28	H	0.051	0.035	0.017				
29	N	-0.146	-0.224	0.077				
30	C	-0.059	-0.077	0.018				

Table S4 Contributions (in %) of individual atoms to the in-gap states in (CdSe)₆-NH₂CH₃.

	Cd 5s ^a	Se 4p ^b	Cd 5s ^c
Spin up	6.11	28.29	59.48
Spin down	5.15	31.75	57.43

^a Contributions from five Cd atoms labeled as 1–5 (see Fig. 1). ^b From six Se atoms labeled as 7–12. ^c From one Cd atom labeled as 6.

Table S5 Amounts of atomic net charge and their changes (in e) of (CdSe)₆-PH₃ and (CdSe)₆-InCl₃ before and after electron injection.

Atomic numbering	Element	(CdSe) ₆ -PH ₃			Element	(CdSe) ₆ -InCl ₃		
		Before	After	Change		Before	After	Change
1	Cd	0.296	0.272	0.024	Cd	0.319	0.246	0.073
2	Cd	0.296	0.261	0.035	Cd	0.311	0.277	0.034
3	Cd	0.245	0.017	0.228	Cd	0.319	0.270	0.050
4	Cd	0.294	0.284	0.011	Cd	0.312	0.282	0.030
5	Cd	0.291	0.274	0.017	Cd	0.305	0.267	0.038
6	Cd	0.291	0.271	0.020	Cd	0.312	0.274	0.038
7	Se	-0.121	-0.144	0.022	Se	-0.093	-0.096	0.003
8	Se	-0.131	-0.135	0.004	Se	-0.201	-0.227	0.027
9	Se	-0.131	-0.127	-0.004	Se	-0.095	-0.141	0.046
10	Se	-0.119	-0.131	0.013	Se	-0.080	-0.152	0.072
11	Se	-0.119	-0.148	0.029	Se	-0.085	-0.102	0.016
12	Se	-0.127	-0.180	0.053	Se	-0.080	-0.149	0.068
13	P	0.126	0.036	0.090	In	0.170	0.105	0.064
14	H	0.011	-0.013	0.023	Cl	-0.162	-0.231	0.069
15	H	0.011	-0.012	0.023	Cl	-0.162	-0.179	0.017
16	H	0.012	-0.012	0.024	Cl	-0.156	-0.222	0.066
17	H	-0.098	-0.128	0.030	H	-0.088	-0.115	0.027
18	H	-0.092	-0.149	0.057	H	-0.102	-0.119	0.017
19	H	-0.097	-0.122	0.024	H	-0.088	-0.125	0.038
20	H	-0.088	-0.141	0.053	H	-0.098	-0.132	0.034
21	H	-0.087	-0.130	0.043	H	-0.098	-0.142	0.044
22	H	-0.091	-0.142	0.051	H	-0.098	-0.106	0.008
23	H	-0.114	-0.154	0.040	H	-0.074	-0.107	0.034
24	H	-0.115	-0.133	0.018	H	-0.074	-0.089	0.014
25	H	-0.115	-0.145	0.030	H	-0.069	-0.064	-0.005
26	H	-0.113	-0.117	0.004	H	-0.076	-0.148	0.072
27	H	-0.116	-0.152	0.036	H	-0.069	-0.073	0.004

Table S6 Contributions (in %) of individual atoms to the in-gap states in $(\text{CdSe})_6\text{-PH}_3$.

	Cd 5s ^a	Se 4p ^b	Cd* 5s ^c
Spin up	7.32	28.80	58.52
Spin down	8.49	25.21	60.53

^a Contributions from five Cd atoms labeled as 1, 3, and 4–6 (see Fig. S8). ^b From six Se atoms labeled as 7–12. ^c From one Cd atom labeled as 3.

Table S7 Changes of atomic net charge (in e) of $(\text{CdSe})_{13}\text{-NH}_2\text{CH}_3$ before and after electron injection.

Atom numbering	Element	Change	Atom numbering	Element	Change
1	Se	-0.001	29	H	0.005
2	Se	0.002	30	H	0.012
3	Se	0.001	31	H	0.002
4	Se	0.022	32	H	0.015
5	Se	-0.029	33	H	-0.007
6	Se	0.012	34	H	0.014
7	Se	0.008	35	H	-0.017
8	Se	0.007	36	H	0.016
9	Se	-0.008	37	H	0.013
10	Se	-0.023	38	H	0.016
11	Se	0.018	39	H	0.011
12	Se	-0.008	40	H	0.049
13	Se	0.018	41	H	-0.009
14	Cd	0.016	42	H	0.000
15	Cd	0.047	43	H	0.012
16	Cd	0.010	44	H	0.034
17	Cd	-0.003	45	H	-0.008
18	Cd	0.033	46	H	0.009
19	Cd	0.058	47	H	0.018
20	Cd	0.085	48	H	0.013
21	Cd	0.018	49	H	0.012
22	Cd	0.038	50	H	0.010
23	Cd	0.033	51	H	0.004
24	Cd	0.069	52	H	-0.001
25	Cd	0.024	53	H	0.012
26	Cd	0.290	54	H	0.012
27	C	0.004	55	H	0.017
28	N	-0.011	56	H	0.007

Table S8 Changes of atomic net charge (in e) of (CdSe)₆-6NH₂CH₃ before and after electron injection.

Atom numbering	Element	Change	Atom numbering	Element	Change
1	Cd	0.051	49	C	0.000
2	Cd	0.071	50	C	-0.002
3	Cd	0.053	51	C	-0.002
4	Cd	0.311	52	C	-0.001
5	Cd	0.072	53	C	-0.001
6	Cd	0.326	54	C	-0.002
7	Se	0.025	55	H	0.006
8	Se	0.010	56	H	-0.003
9	Se	0.002	57	H	0.009
10	Se	0.004	58	H	0.010
11	Se	-0.054	59	H	0.001
12	Se	0.008	60	N	0.001
13	H	-0.004	61	C	-0.002
14	H	0.004	62	H	0.006
15	H	-0.003	63	H	-0.002
16	H	0.015	64	H	0.007
17	H	-0.007	65	H	0.008
18	H	0.007	66	H	0.001
19	H	-0.007	67	N	0.002
20	H	0.011	68	C	-0.002
21	H	0.014	69	H	0.008
22	H	-0.011	70	H	0.000
23	H	0.003	71	H	0.007
24	H	0.001	72	H	0.013
25	H	0.002	73	H	0.001
26	H	0.011	74	N	0.002
27	H	-0.002	75	C	-0.004
28	H	0.002	76	H	-0.029
29	H	0.001	77	H	0.038
30	H	0.002	78	H	-0.032
31	H	0.011	79	H	0.005
32	H	-0.001	80	H	0.019
33	H	0.004	81	N	0.005
34	H	0.001	82	C	0.002
35	H	0.004	83	H	0.009
36	H	0.012	84	H	-0.001
37	H	-0.005	85	H	0.007
38	H	0.003	86	H	0.007
39	H	0.000	87	H	-0.020
40	H	0.003	88	N	0.002
41	H	0.011	89	C	0.010

42	H	-0.002	90	H	0.008
43	N	-0.007	91	H	-0.001
44	N	-0.011	92	H	0.006
45	N	-0.010	93	H	0.011
46	N	-0.007	94	H	-0.021
47	N	-0.006	95	N	0.001
48	N	-0.008	96	C	0.009

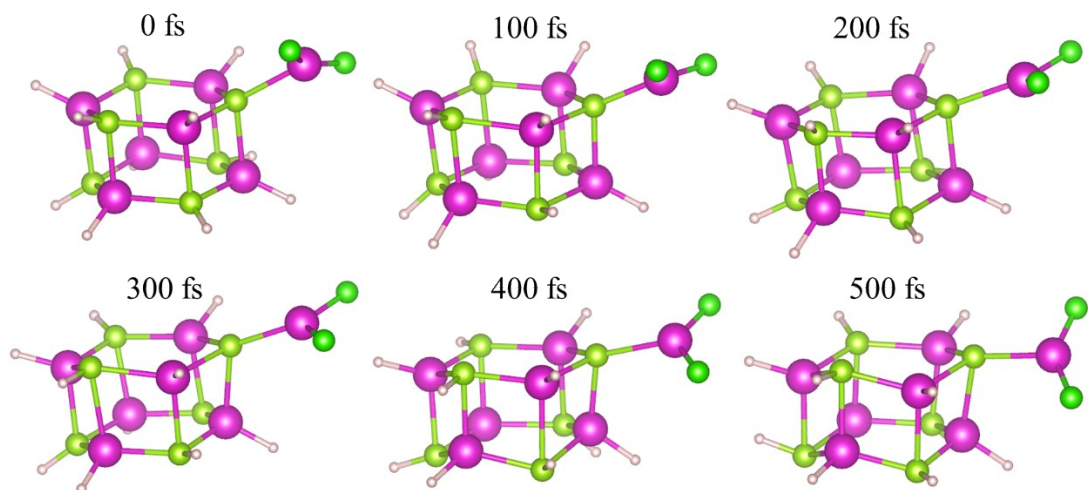


Fig. S1 Structure variations in $(\text{CdSe})_6\text{-CdCl}_2$ after electron injection as a function of time.

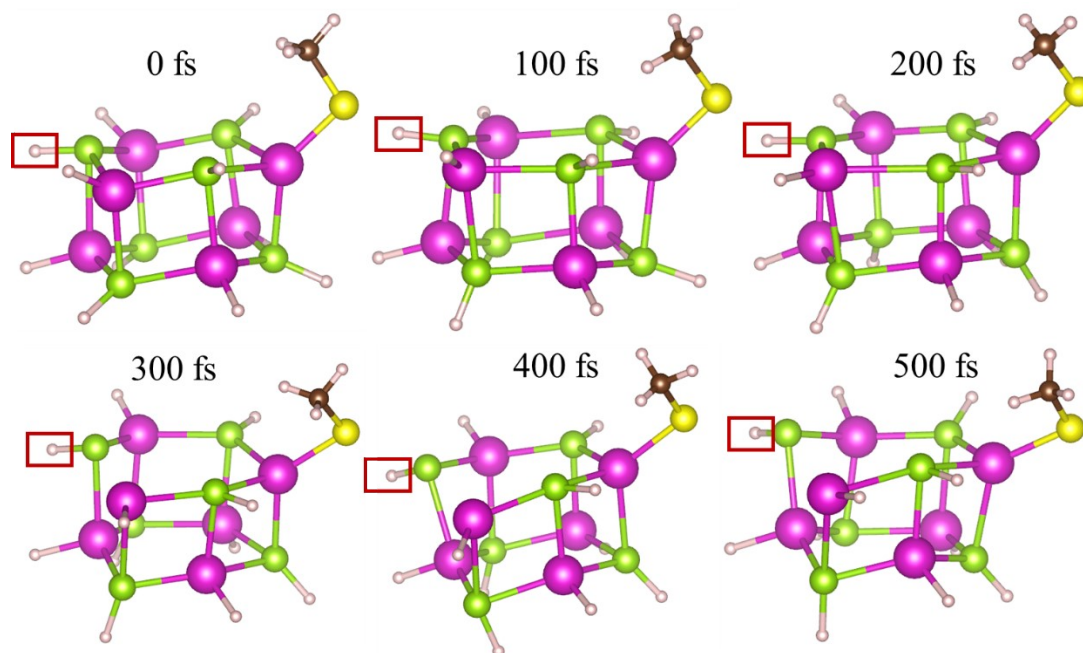


Fig. S2 Structure variations in (CdSe)₆-SCH₃-H (a) after electron injection as a function of time.

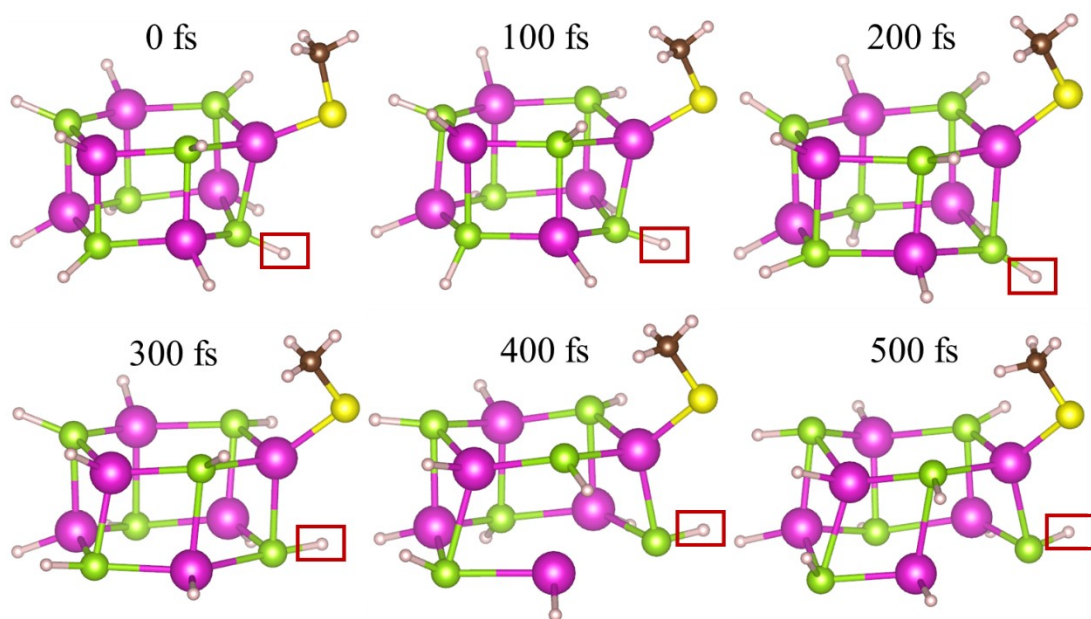


Fig. S3 Structure variations in (CdSe)₆-SCH₃-H (b) after electron injection as a function of time.

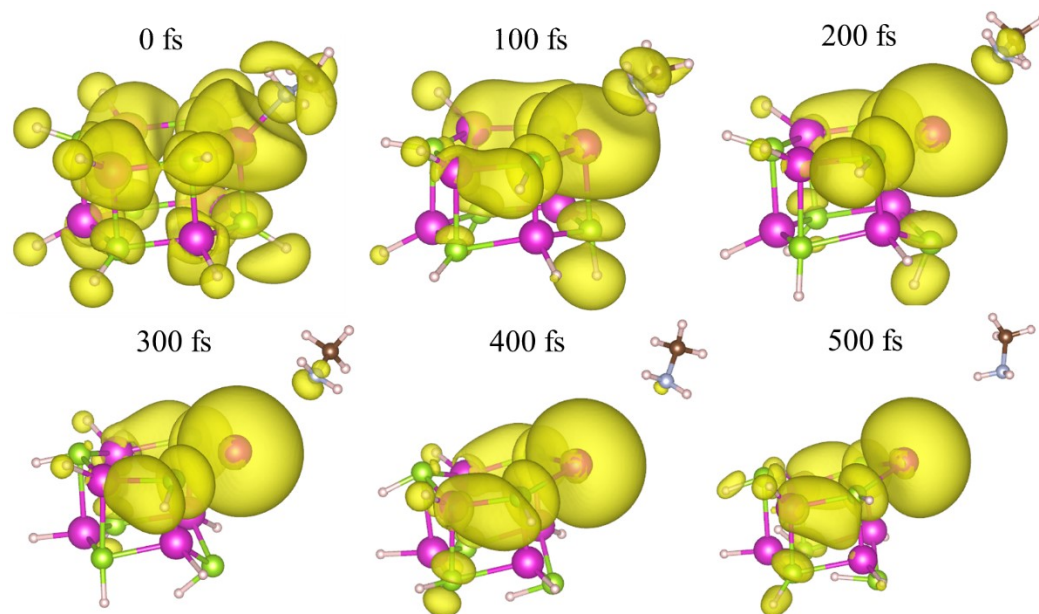


Fig. S4 Variation of the spin-down LUMO of (CdSe)₆-NH₂CH₃ as a function of time.

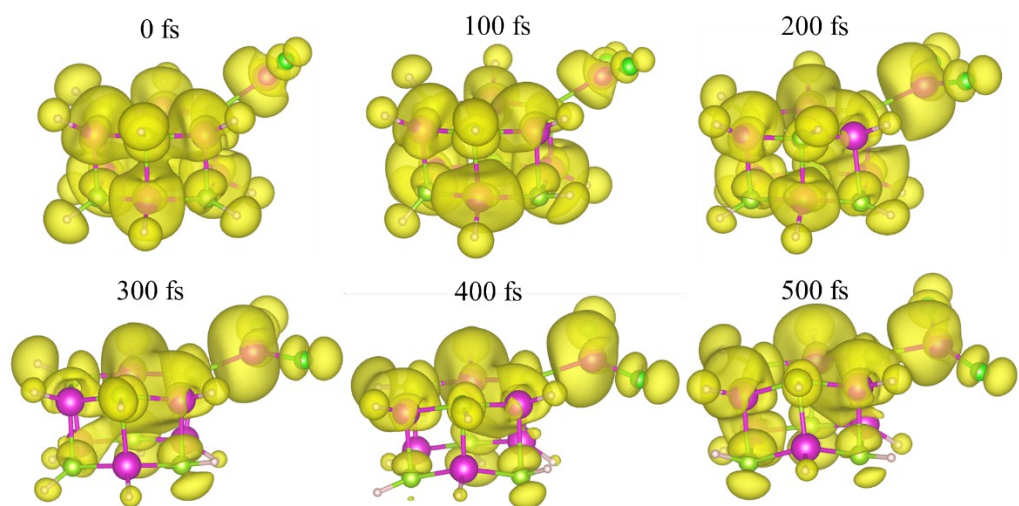


Fig. S5 Variation of the spin-up LUMO of (CdSe)₆-CdCl₂ as a function of time.

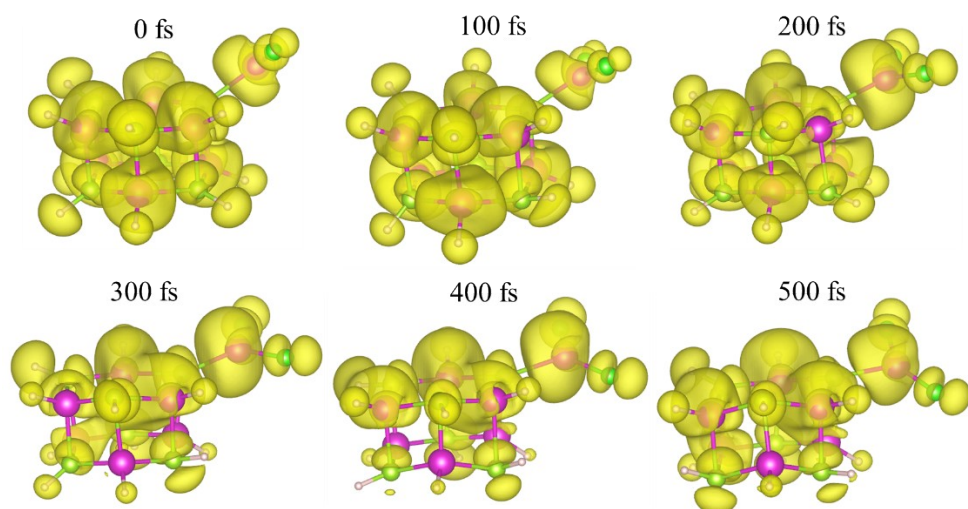


Fig. S6 Variation of the spin-down LUMO of (CdSe)₆-CdCl₂ as a function of time.

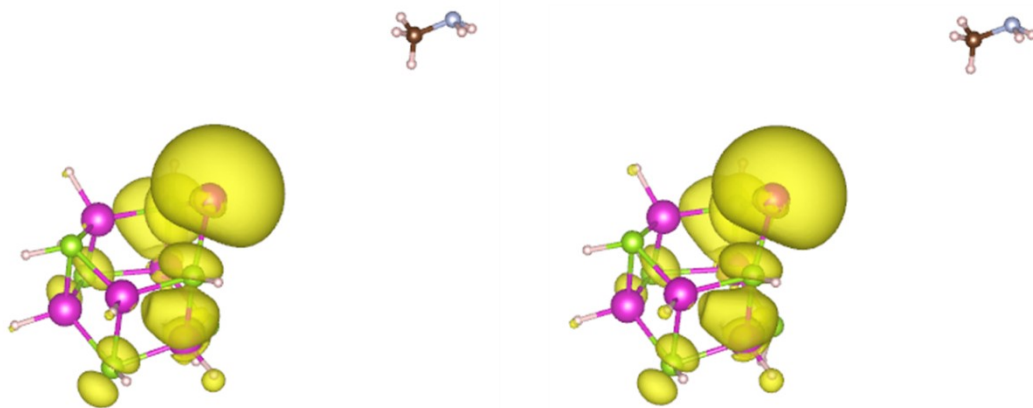


Fig. S7 Spin-up (Left) and spin-down (Right) LUMO of (CdSe)₆-NH₂CH₃ as 1 ns.

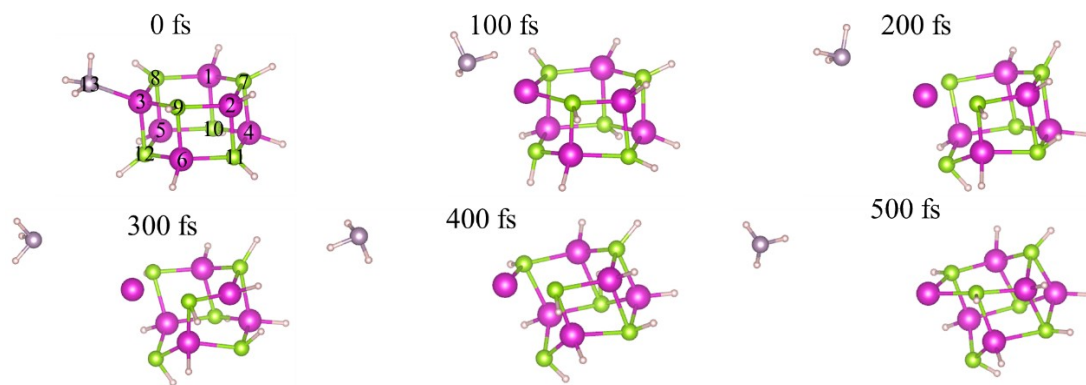


Fig. S8 Structure variations in $(\text{CdSe})_6\text{-PH}_3$ after electron injection as a function of time.

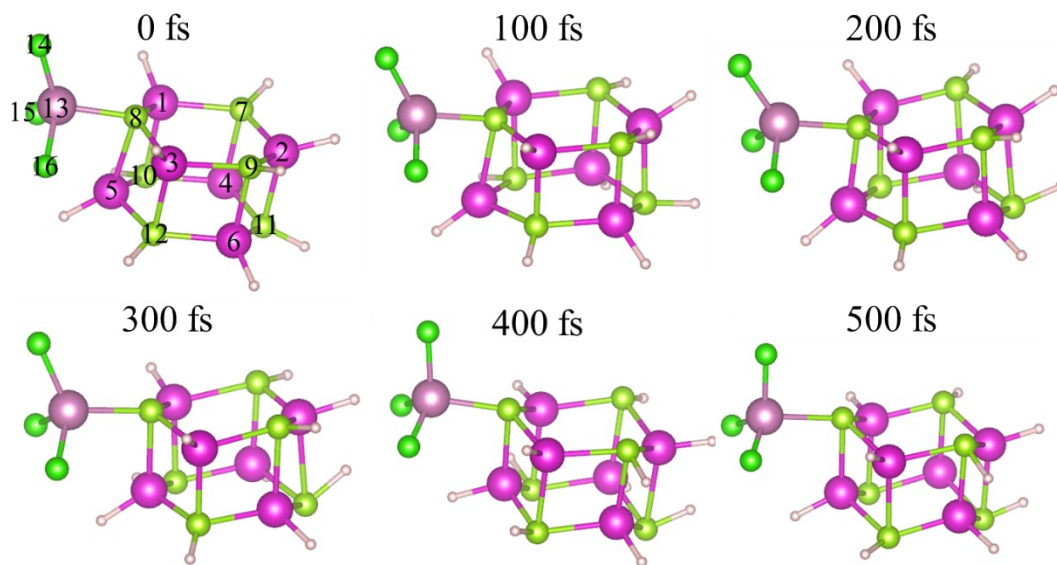


Fig. S9 Structure variations in $(\text{CdSe})_6\text{-InCl}_3$ after electron injection as a function of time.

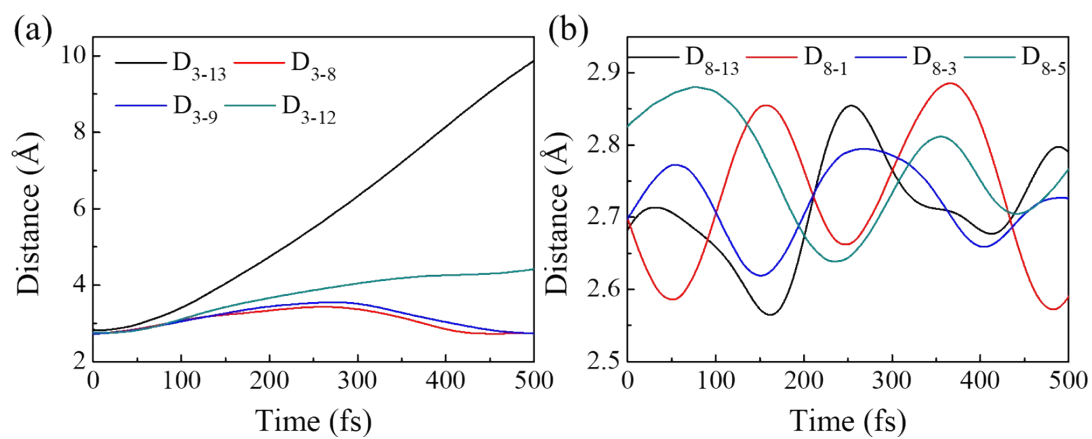


Fig. S10 Variation of selected bond lengths in (a) $(\text{CdSe})_6\text{-PH}_3$ and (b) $(\text{CdSe})_6\text{-InCl}_3$ as a function of time.

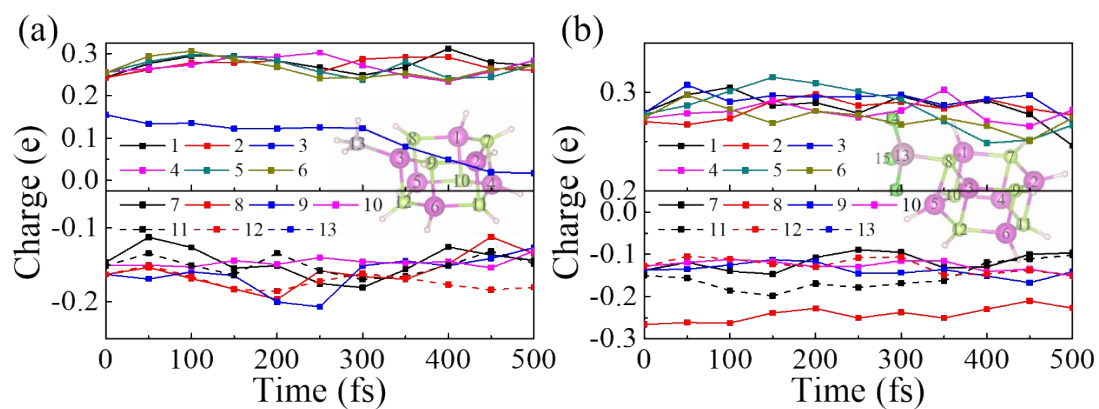


Fig. S11 Changes of atomic net charge for Cd (top) and Se/P/In (bottom) atoms in (a) $(\text{CdSe})_6\text{-PH}_3$ and (b) $(\text{CdSe})_6\text{-InCl}_3$ with time after electron injection.

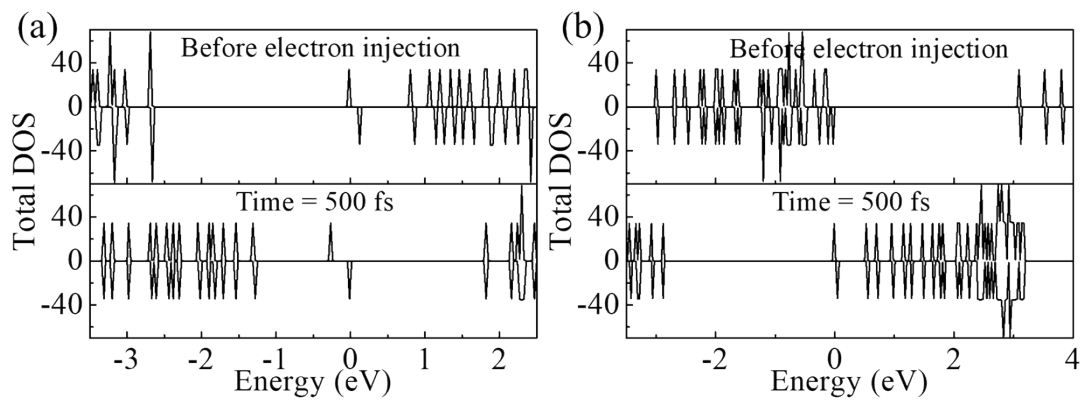


Fig. 12 Total DOS of (a) $(\text{CdSe})_6\text{-PH}_3$ and (b) $(\text{CdSe})_6\text{-InCl}_3$ before and after electron injection. The Fermi level is set to 0 eV.

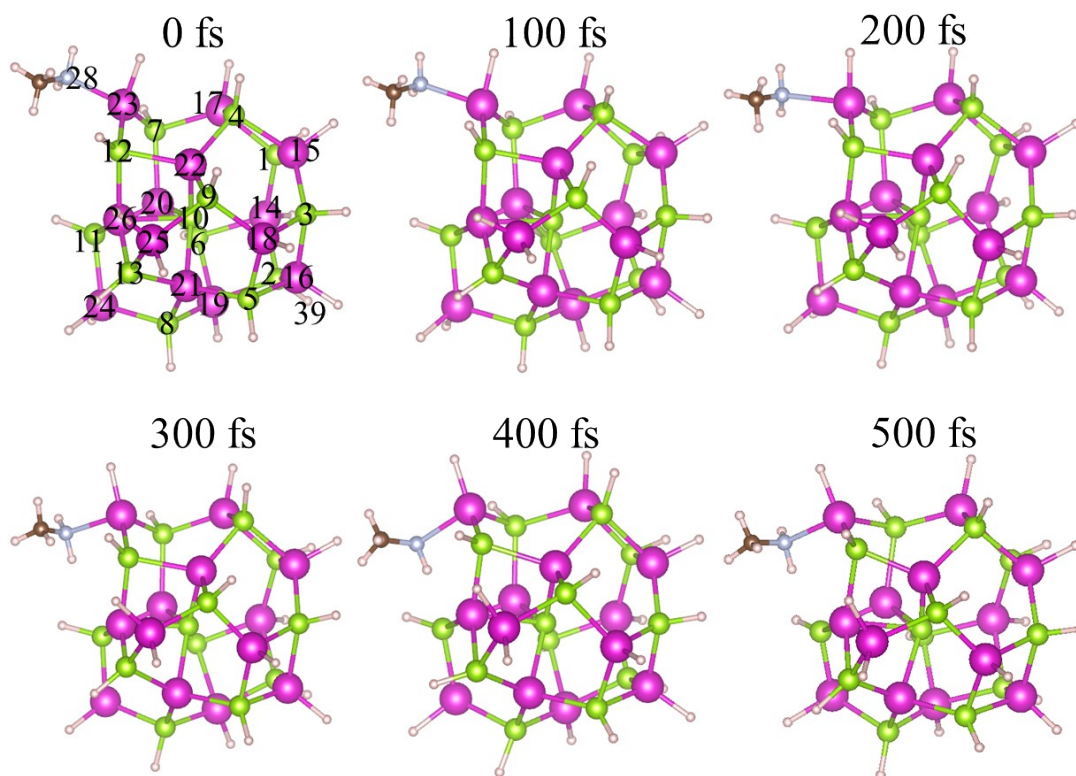


Fig. S13 Structure variations in (CdSe)₁₃-NH₂CH₃ after electron injection as a function of time.

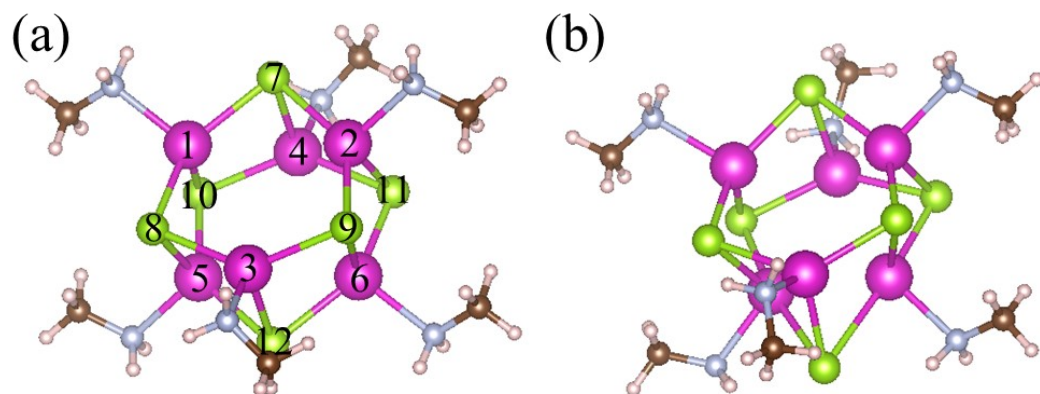


Fig. S14 Optimized structure of $(\text{CdSe})_6\text{-}6\text{NH}_2\text{CH}_3$ (a) before and (b) after electron injection.

References

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