

Supporting Information

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Probing the Edges between Stability and Degradation of
a Series of ZnSe-Based Layered Hybrid Semiconductors

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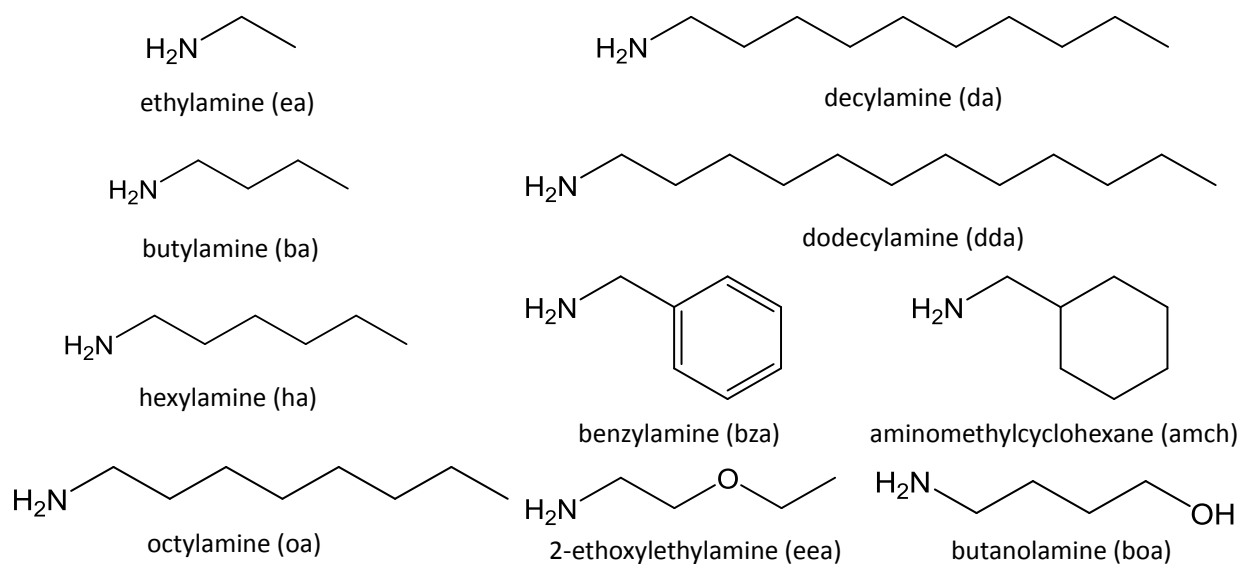
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Scheme S1. Structures and abbreviations of all organic ligands discussed in this work.

$$\frac{x \times M_L + (1 - x) \times M_{ba}}{M_{ZnSe} + x \times M_L + (1 - x) \times M_{ba}} \times 100\% = \text{TGA wt\% loss}$$

Equation S1. Equation describing ligand-exchange yield (LEY) of ligand exchange reactions described in the main text. M_L is the molar mass of the exchanged ligand, M_{ba} is the molar mass of butylamine (73.14 g/mol), M_{ZnSe} is the molar mass of ZnSe (144.35 g/mol), x is the mole fraction of the newly introduced ligand incorporated into the reaction product, and $(1-x)$ is the mole fraction of butylamine remaining in the reaction product.

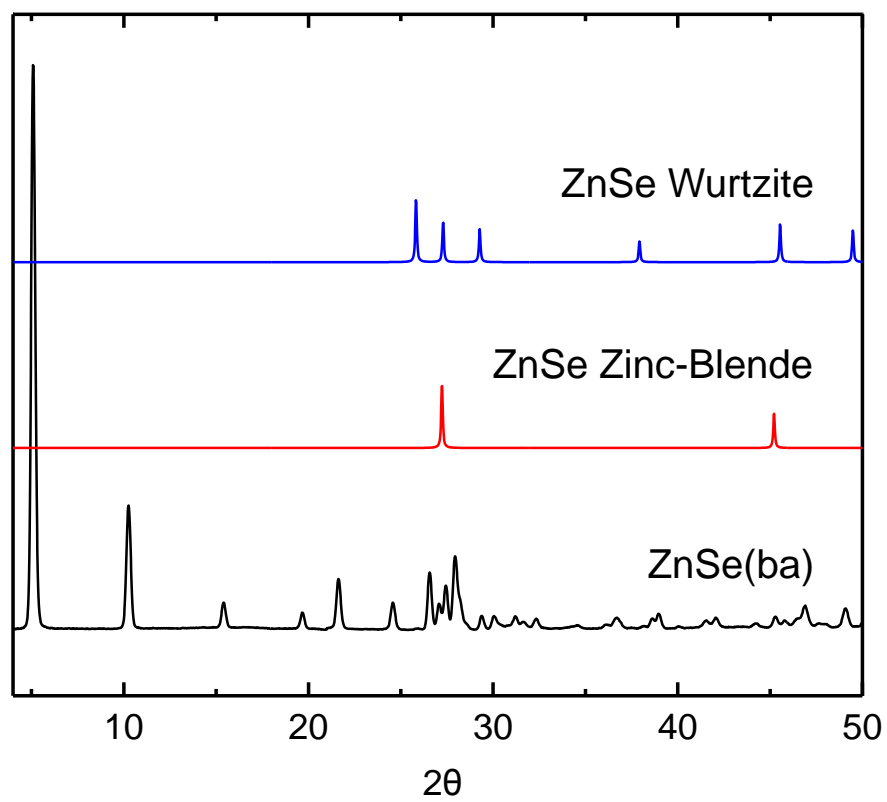


Figure S1. Comparison of powder XRD patterns of wurtzite ZnSe, zinc blende ZnSe, and ZnSe(ba).

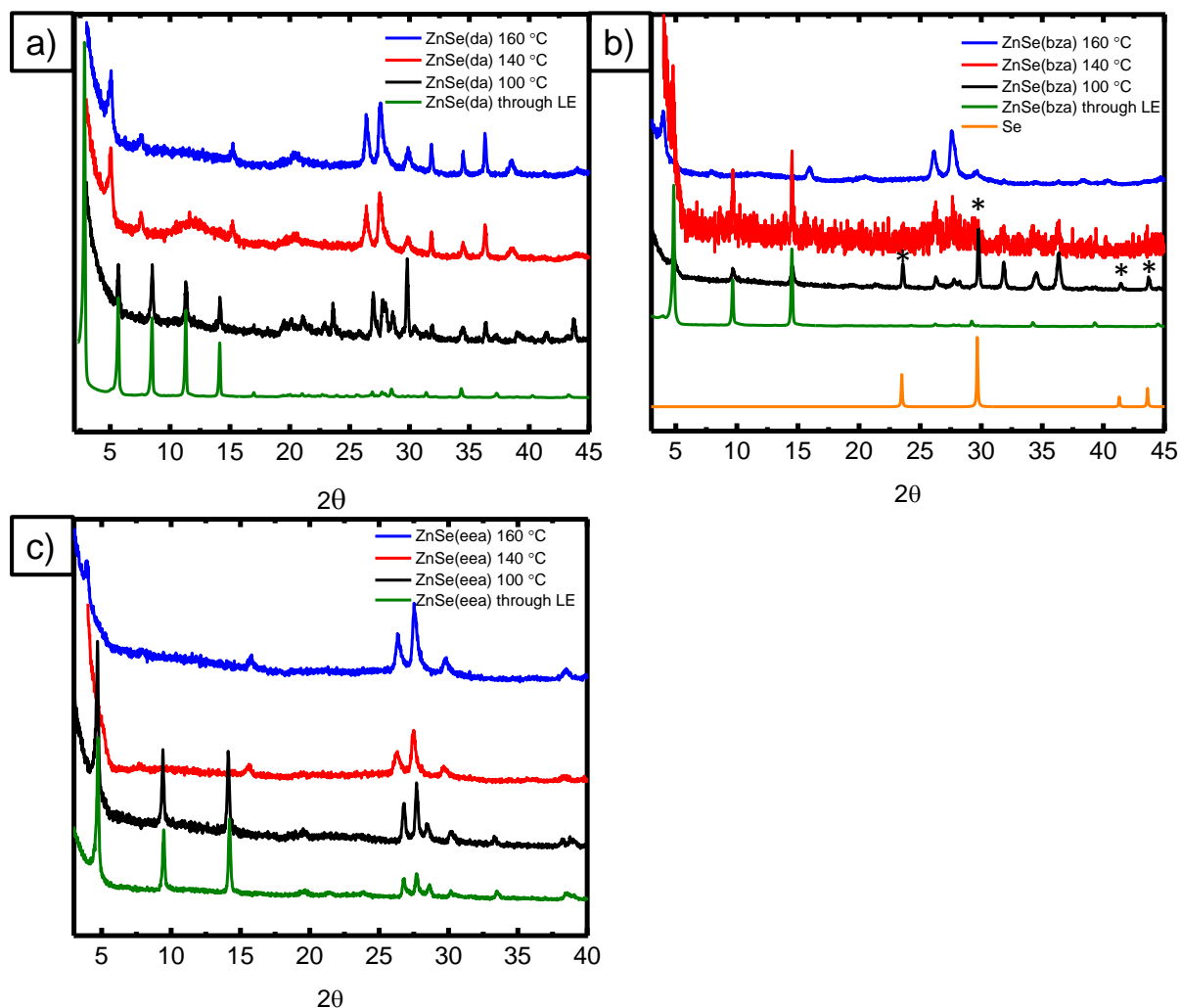


Figure S2. Powder X-ray diffractograms of a) ZnSe(da), b) ZnSe(bza) and c) ZnSe(eea) synthesized at 100 °C (black), 140 °C (red), or 160 °C (blue) by incubation of ZnCl_2 and Se in the corresponding amine at autogenous pressure. Attempts to form ZnSe(da) at all three temperatures yielded material showing poor crystallinity (broad reflections) and shifts in diffraction angles relative to those observed in the corresponding material formed by ligand exchange (green). The black asterisks (*) in panel (b) indicate the reflections matching those of elemental Se (orange), suggesting the presence of unreacted Se after attempts to synthesize ZnSe(bza) at 100 °C. At 140 and 160 °C, poor crystallinity and poor agreement with the expected diffraction pattern were observed. ZnSe(eea) was obtainable by synthesis at 100 °C, but unknown phases were obtained at 140 and 160 °C.

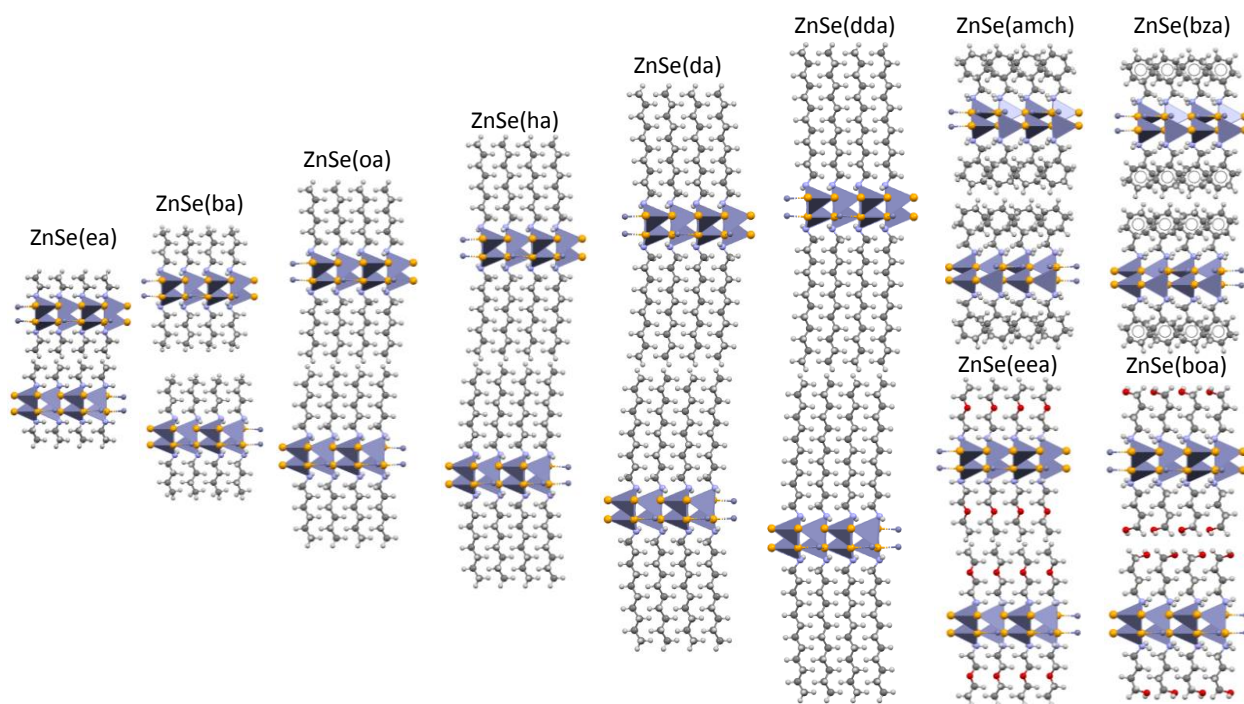


Figure S3. Simulated models of all ZnSe(L) LHs simulated in this work, viewed along the crystallographic *b*-axis (Zn, teal polyhedra; Se, orange; N, blue; O, red; C, gray; H, white).

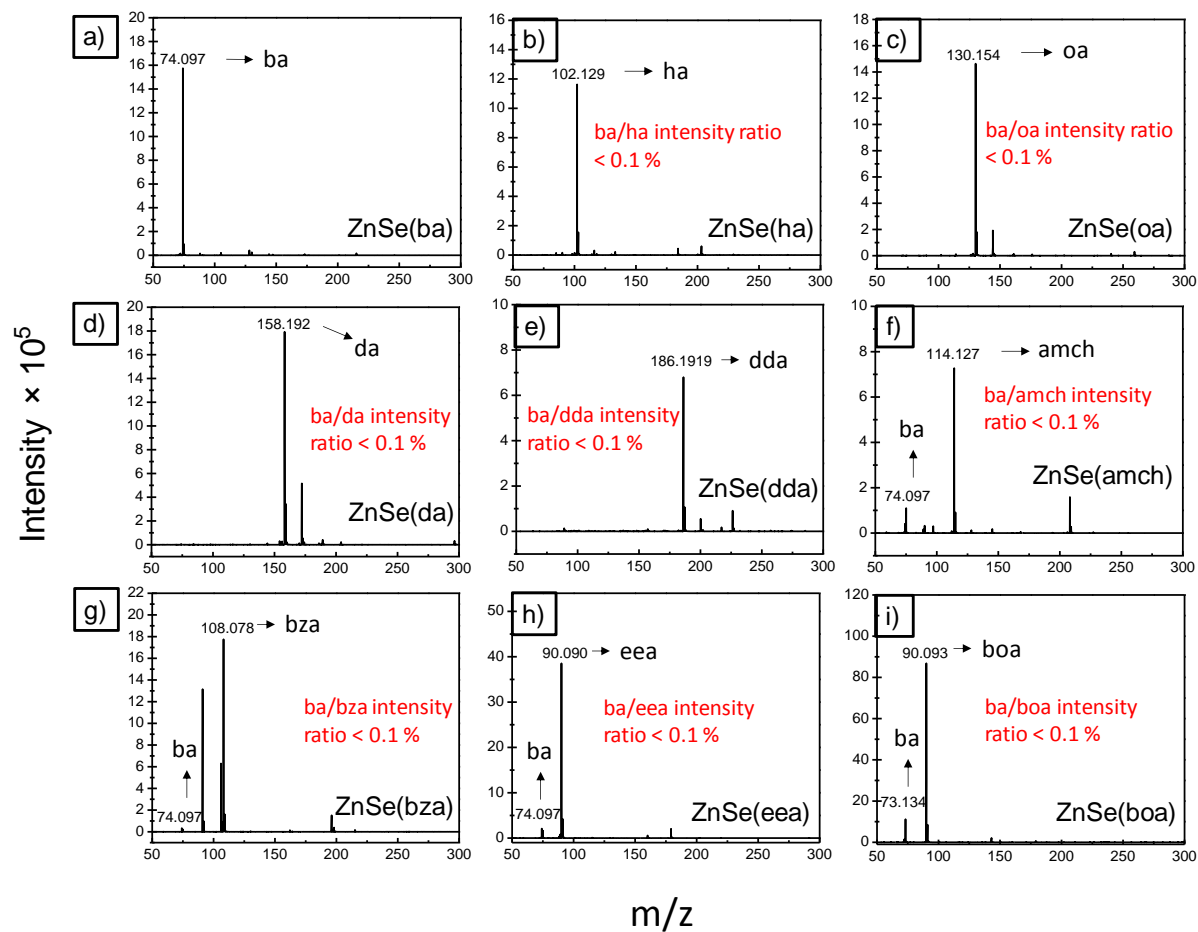


Figure S4. Direct analysis in real time mass spectrometry (DART-MS) analysis of all ZnSe-based LHs discussed in this work.

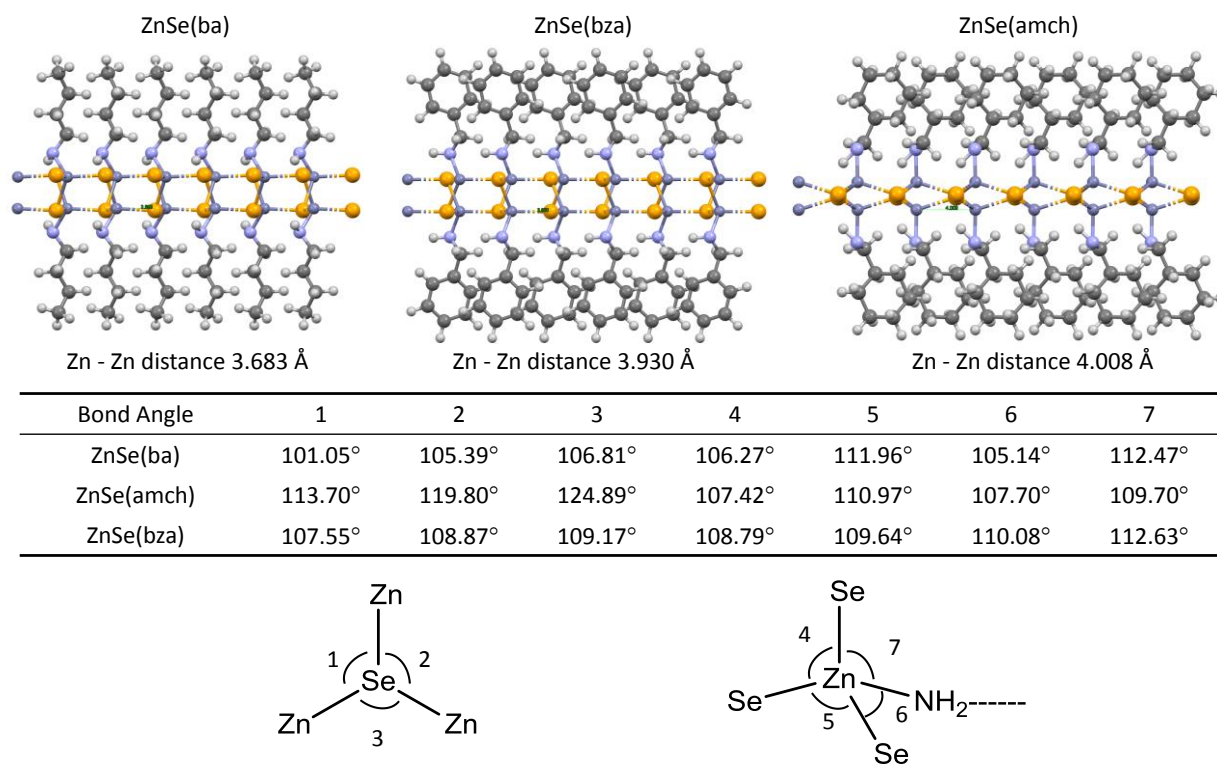


Figure S5. Bond angle and bond distance information of simulated ZnSe(ba), ZnSe(bza) and ZnSe(amch). Models constructed with Materials Studio 8.0 as described in the Experimental Section of the main text. Models viewed along crystallographic a -axis (Zn, teal dark blue; Se, orange; N, light blue; C, gray; H, white).

Nature of coordination interaction between boa and the ZnSe surface

Periodic, plane wave DFT calculations using the Quantum ESPRESSO software package^[1] were used to compare the energies of boa bound to the 2D ZnSe slab *via* the hydroxide O atom and the amine N atom. Electron correlation and exchange interactions were incorporated using the PBE generalized gradient approximation^[2] and core-valance electron interactions were represented using scalar relativistic ultrasoft pseudopotentials.^[3] Although PBE0 was used for the isolated ZnSe system in the main text, GGAs can provide a sufficient description of ground-state properties for solid state systems at a lower computational cost.^[4] Dispersion interactions were incorporated using the empirical Grimme D3 correction.^[5] All calculations with Quantum ESPRESSO employed a 3×3×1 Monkhorst-Pack *k*-space grid^[6] to sample over the Brillouin zone and a 60 Ry kinetic energy plane-wave cutoff. A geometry optimization using 10⁻⁴ Hartree/bohr force convergence criteria (including relaxation of the orthorhombic lattice) was performed on a single 1×1×1 unit cell with the hydroxide terminating group coordinating with the ZnSe surface *via* the O atom. The obtained cell dimensions were then kept fixed while geometry optimizing the system with the opposite orientation of the ligand (with the amine terminating group coordinating with ZnSe *via* the N atom). Initial geometries for ZnSe(boa) (with either -NH₂ or -OH coordinated to the inorganic slab) were obtained using Materials Studio 8.0 and geometry optimized using the Universal Force Field as described in the main text.

Several interaction energies were computed using a 2×2×1 3D periodic supercell consisting of 608 atoms. Even though each supercell repeats the unit cell twice along the *x* and *y* Cartesian directions and only once in the *z* direction, a single 1×1×1 unit cell includes two ZnSe layers with 2 ligands above and below each layer for a total of 8 ligands. Given that the length of the supercell along the *z*-direction is approximately 36 Å, *k*-point integration was not needed along this axis beyond the gamma point. Figure S5 depicts the atoms used in each interaction energy calculation. The interaction energy of a single ligand with the remaining atoms in the supercell, $\Delta E_{\text{ligand-supercell}}$, was computed by subtracting the energy of a supercell having a single ligand absence ($E_{\text{supercell}(31)}$) and the energy the ligand alone ($E_{\text{ligand}(1)}$) from the energy of the complete supercell ($\Delta E_{\text{supercell}(32)}$), where the subscripts denote the total number of ligands present in the supercell:

$$\Delta E_{\text{ligand-supercell}} = E_{\text{supercell}(32)} - E_{\text{ligand}(1)} - E_{\text{supercell}(31)} ,$$

The interaction energy between a single ligand and the remaining 31 (periodic) ligands, without the ZnSe slab present, $\Delta E_{\text{ligand-ligand}}$, was computed in a similar fashion by subtracting $E_{\text{ligand}(1)}$ and the remaining 31 ligands ($E_{\text{ligand}(31)}$) from a system of all 32 ligands ($E_{\text{ligand}(32)}$):

$$\Delta E_{\text{ligand-ligand}} = E_{\text{ligand}(32)} - E_{\text{ligand}(1)} - E_{\text{ligand}(31)} .$$

The overall Interaction energies between the terminating group (-NH₂ or -OH) and the ZnSe surface, $\Delta E_{\text{ligand-ZnSe}}$, was hence calculated by the difference of the two interaction energies calculated above:

$$\Delta E_{\text{ligand-ZnSe}} = \Delta E_{\text{ligand-supercell}} - \Delta E_{\text{ligand-ligand}} .$$

Figure S6 summarizes the average of these ligand interaction energy calculations determined at each of the 8 distinct ligand positions within a 1×1×1 cell. These calculations indicate that the boa ligands having their -NH₂ groups coordinated to Zn²⁺ exhibit close to 50% more favorable interaction with the supercell

than those with their -OH groups bound to the ZnSe slab. The increased interaction with the ZnSe slab alone, $\Delta E_{\text{ligand-ZnSe}}$, for the amine group coordinated with the ZnSe surface indicates that Zn-N bonding is preferred over Zn-O bonding at the material surface. Additionally, the increased interaction with neighboring ligands, $\Delta E_{\text{ligand-ligand}}$, also indicates that interlayer ligand interactions play a significant role in the preference for -NH₂ groups binding to the ZnSe slab.

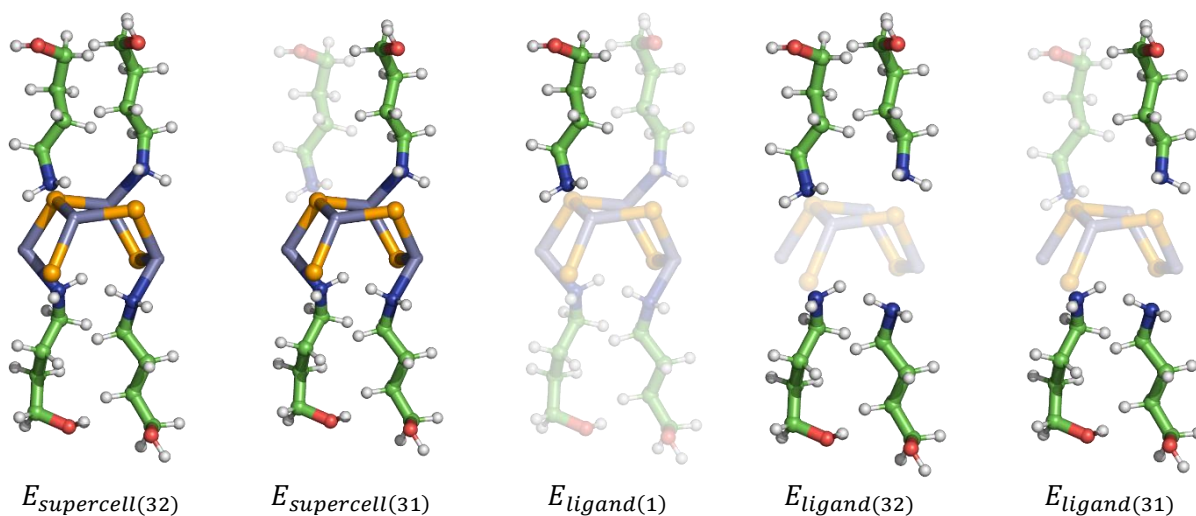


Figure S6. Combinations of atoms present in the 2x2x1 boa-ZnSe supercell used to compute the interaction energies described above. Only half of a 1x1x1 unit cell is shown for clarity. Faded atoms depict those that are absent from the calculation.

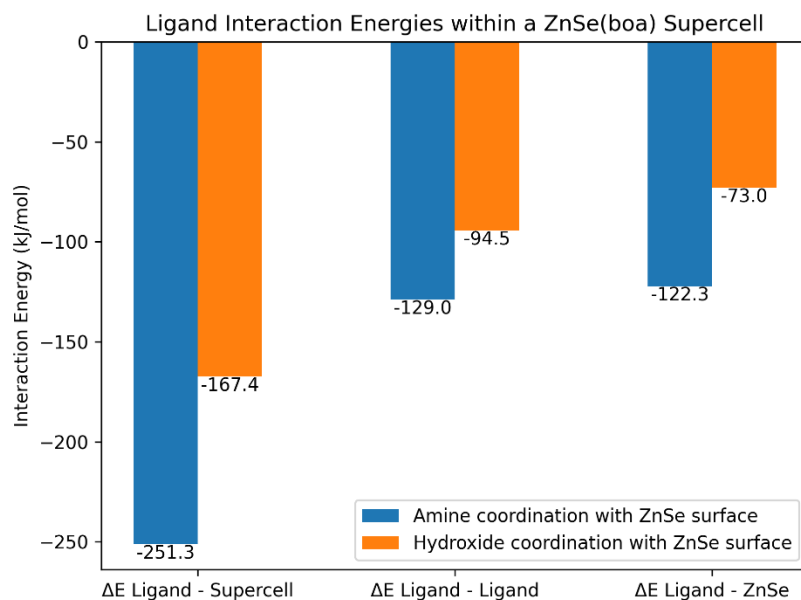


Figure S7. Ligand interaction energies in ZnSe(boa) calculated as described in the text above. Interaction energies were calculated for each of 8 ligand positions in a single 1×1×1 cell. Error bars, calculated as a single standard deviation from the mean, are not shown as they are less than 1 kJ/mol in all cases.

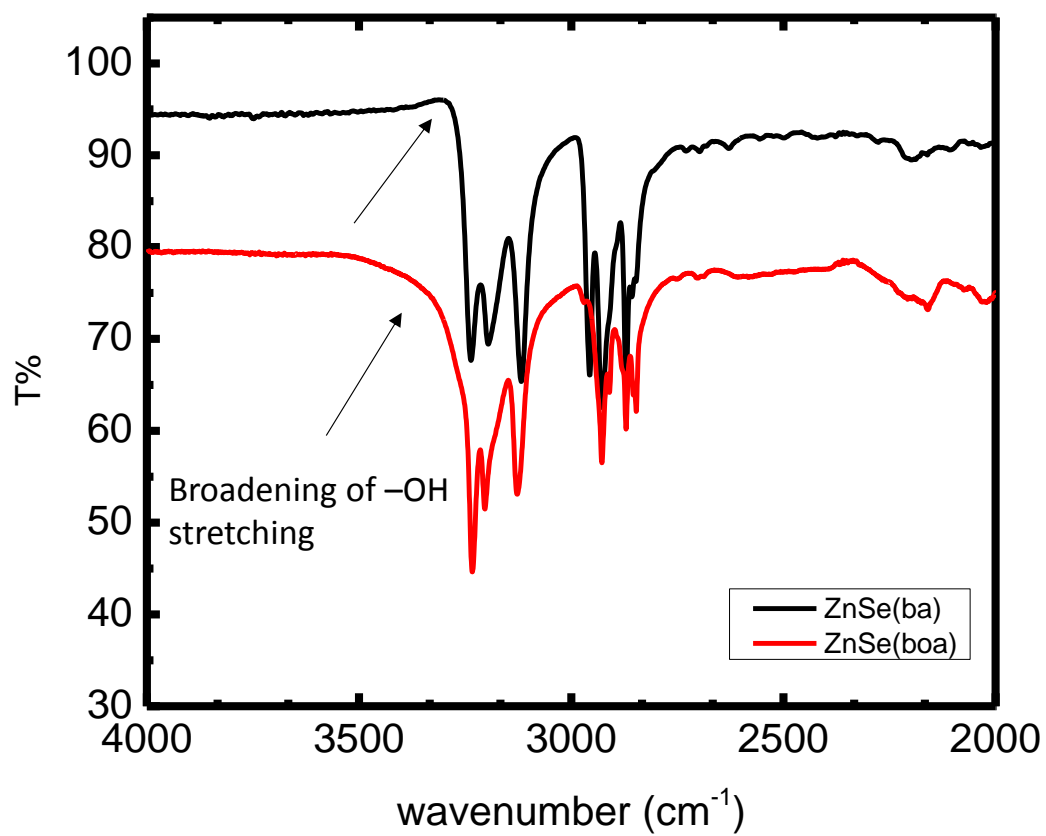


Figure S8. Fourier-transform infrared spectroscopy (FTIR) of ZnSe(boa) (red) and ZnSe(ba) (black). The broad feature at around 3300 cm^{-1} attributed to the O-H stretch of the hydroxyl functional group of boa.

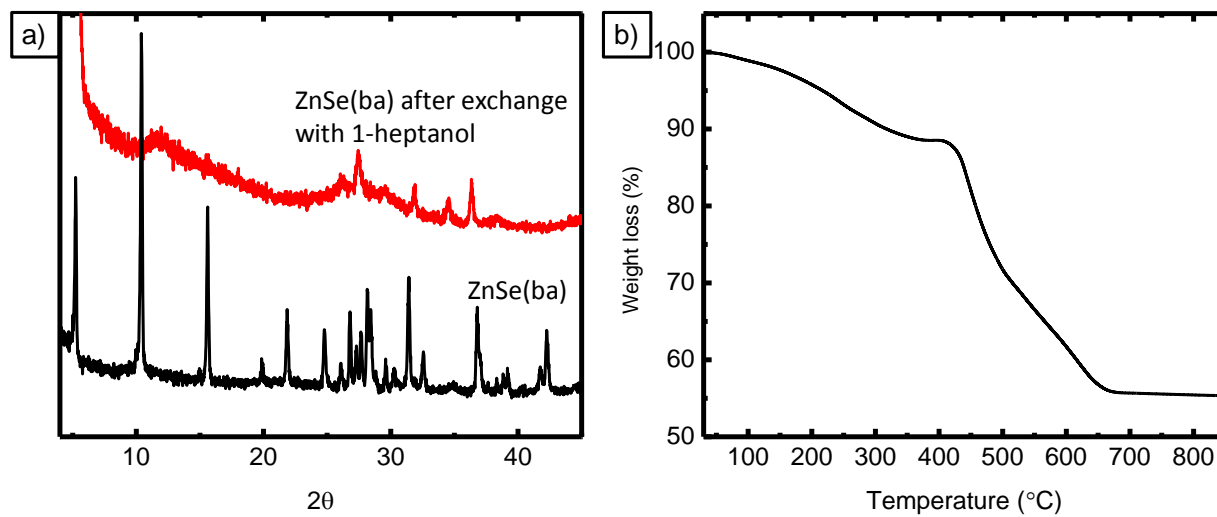


Figure S9. a) Powder X-ray diffractogram and b) thermogravimetric analysis of ZnSe(ba) after incubation at 140 °C in neat heptanol for 5 days.

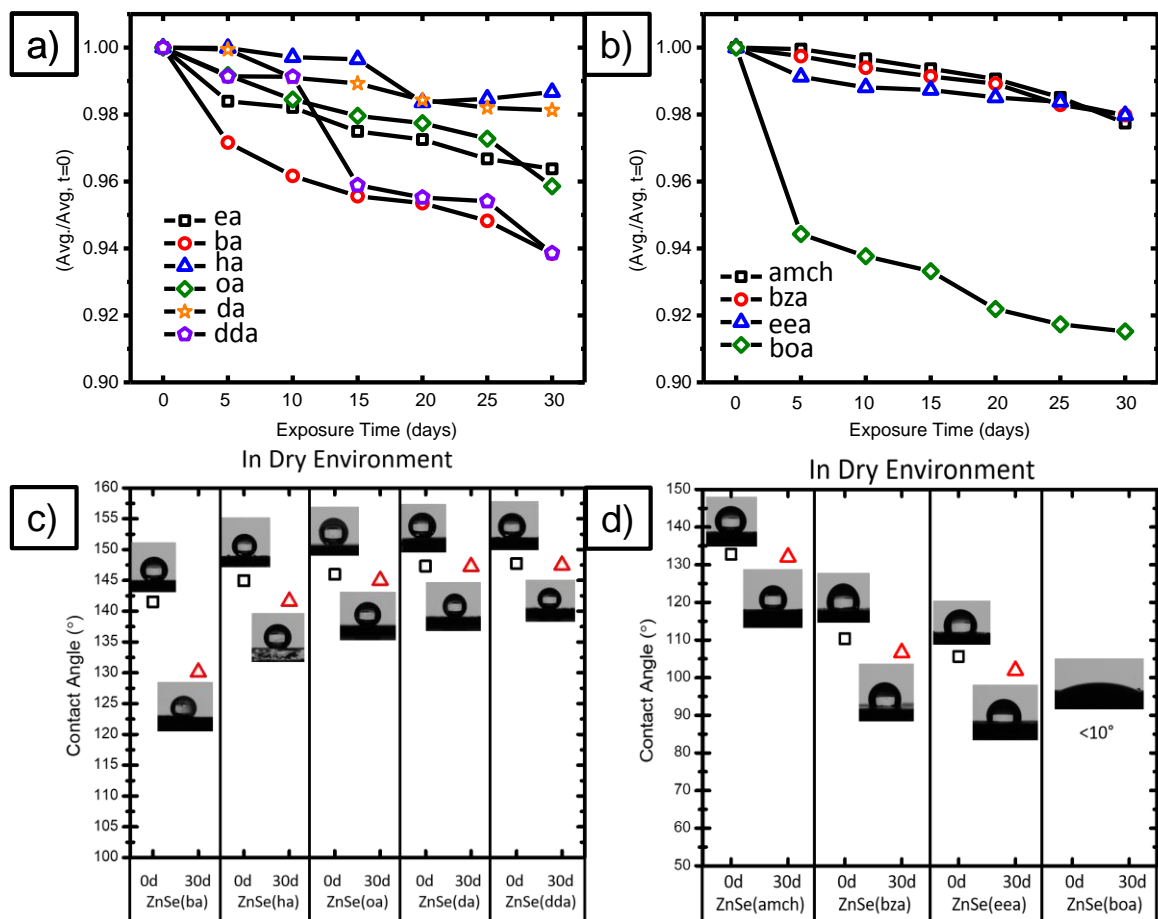


Figure S10. a, b) Normalized average of diffuse reflectance in the visible range (400-700 nm) of all ligand exchanged LHCs incubated over a period of 30 days in a <0.1% RH environment at room temperature. c, d) Contact angle measurement of all ligand-exchanged samples before and after incubating for 30 days in a <0.1% R.H. dry environment at room temperature.

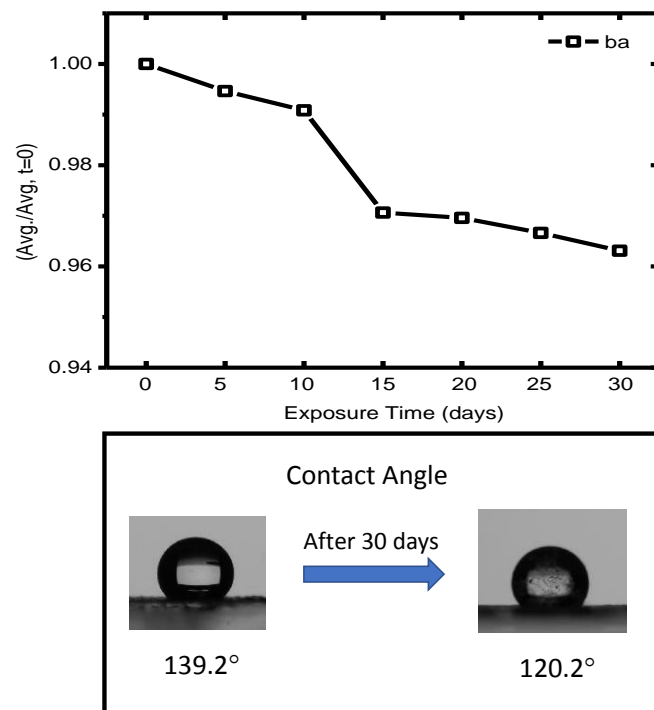


Figure S11. DRS (top) and CA (bottom) data for ZnSe(ba) exposed to a O_2 -free 50% R.H. environment over a period of 30 days.

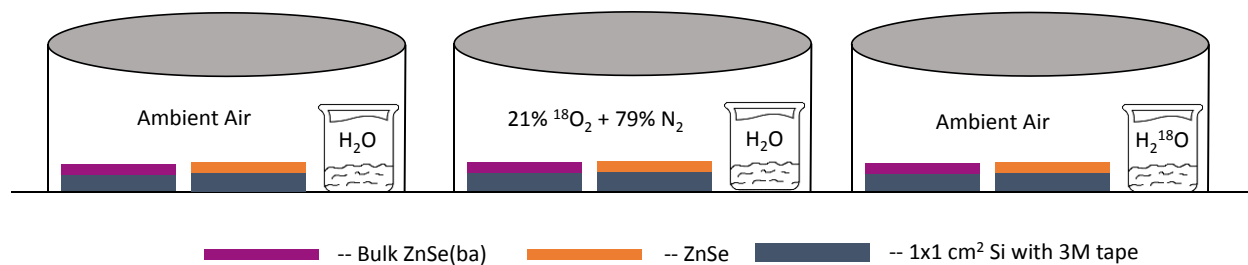


Figure S12. Schematic of environmental exposure experiments used to prepare samples for analysis by D-SIMS. ZnSe and ZnSe(ba) were placed into three different sealed chambers with the environments shown in the schematic above.

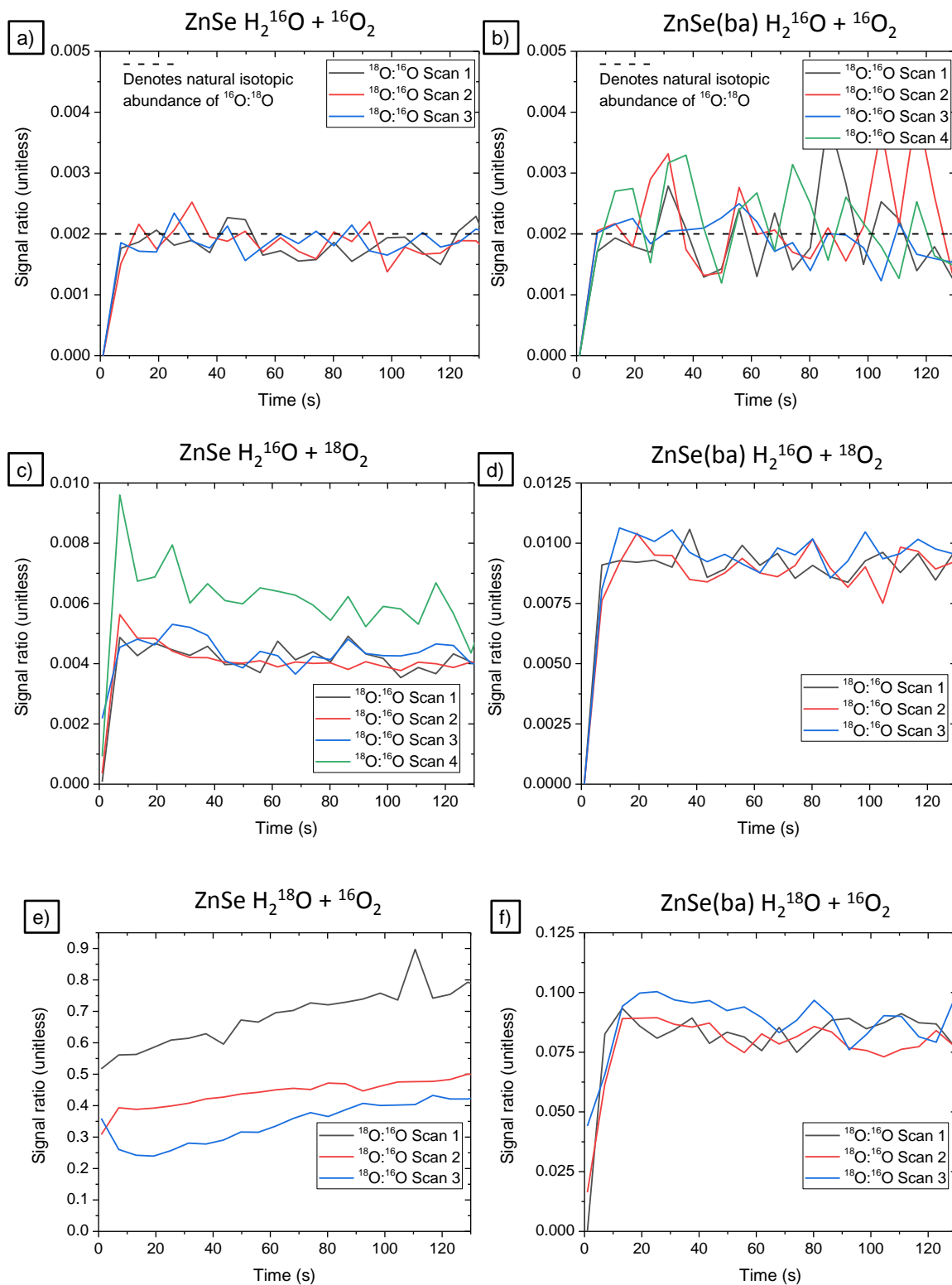


Figure S13. Ratios of $^{18}\text{O}:^{16}\text{O}$ obtained from three D-SIMS depth profiles of 120 s each of ZnSe and ZnSe(ba) exposed to a control (a and b) environment or environments having $^{18}\text{O}_2$ (c and d) or $^{18}\text{H}_2\text{O}$ (e and f).

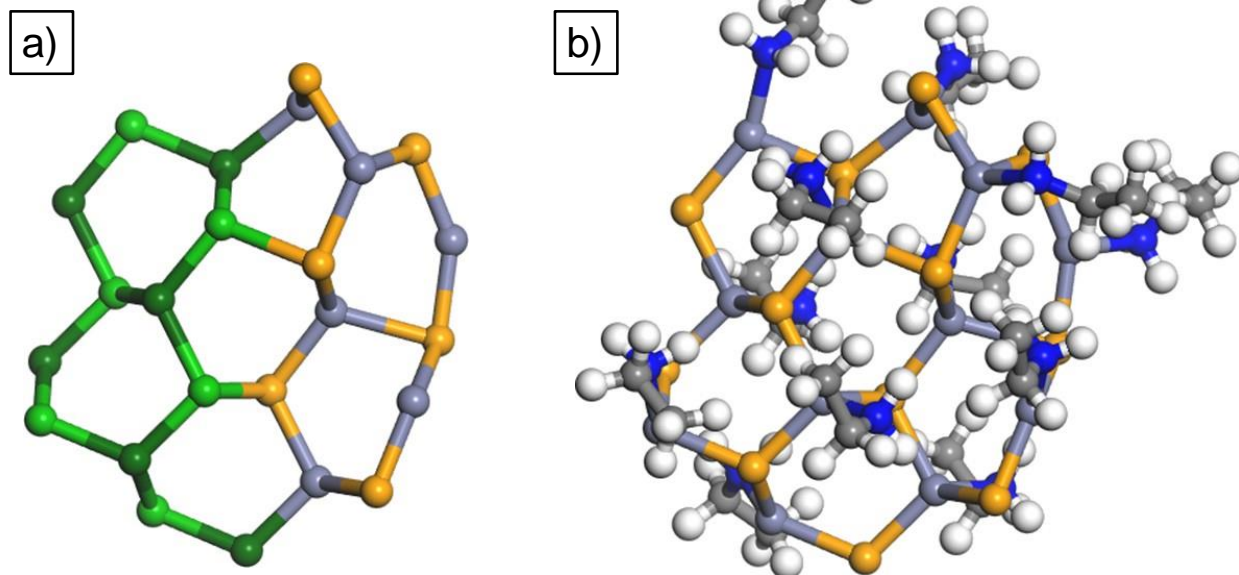


Figure S14. a) Fragment of ZnSe(ea) used for degradation pathway calculations depicted in Figure 4 of the main text. Atoms that were fixed during geometry optimization are depicted in light (Zn) and dark (Se) green. Ligands omitted for clarity. b) Fragment of ZnSe(ea) used for degradation pathway calculations depicting ligands.

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