Electronic Supplementary Material (ESI) for Materials Horizons. This journal is © The Royal Society of Chemistry 2020

Supporting Information

Anisotropic 2D Excitons Unveiled in Organic-Inorganic Quantum Wells

Lorenzo Maserati[†]*, Sivan Refaely-Abramson^{†‡*, Christoph Kastl[†], Christopher T. Chen[†],}

Nicholas J. Borys[†], Carissa N. Eisler^{†§}, Mary S. Collins[†], Tess E. Smidt^{†‡¶}, Edward S. Barnard[†],

Matthew Strasbourg^{\perp}, *Elyse A. Schriber*^{\dagger}, *Brian Shevitski*^{\dagger ‡}, *Kaiyuan Yao*^{$\dagger \nabla$}, *J. Nathan Hohman*^{\dagger},

P. James Schuck^{$\dagger \nabla$}, Shaul Aloni^{\dagger}, Jeffrey B. Neaton^{$\dagger \ddagger \# *$}, and Adam M. Schwartzberg^{$\dagger *$}

[†] The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

[‡] Department of Physics, University of California Berkeley, Berkeley, CA 94720, USA.

[§] Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, USA.

¹ Department of Physics, Montana State University, Bozeman MT, 59717, USA.

^v Department of Mechanical Engineering, Columbia University, New York City, 10027 NY,

USA

[¶] Kavli Energy Nanosciences Institute at Berkeley, Berkeley, CA 94720, USA.

Correspondence to: <u>lmaserati@lbl.gov</u>, <u>sivan.refaely-abramson@weizmann.ac.il</u>, jbneaton@lbl.gov, amschwartzberg@lbl.gov

1.	Figure S1:	Steady state absorption spectrum of $[AgSePh]_{\infty}$
2.	Figure S2:	Transient absorption amplitude fluence dependence in $[AgSePh]_{\infty}$ S4
3.	Figure S3:	Ultrafast transient absorption dynamics for varying excitation energy S5
4.	Figure S4:	Atomic force microscopy of $[AgSePh]_{\infty}singlecrystals$ and NC films . S6
5.	Figure S5:	GIWAXS 2D map of $[AgSePh]_{\infty}$ NC film
6.	Figure S6:	P-XRD area detector images of NC film and micron-size crystals S8
7.	Figure S7:	Comparison NC film vs. single crystal absorption coefficient

8.	Figure S8: PL maps of of NC film and micron-size crystals	S9
9.	Figure S9: Schematic of the back focal plane (BFP) model	S10
10.	Figure S10: Schematic of the optical system for BFP imaging	S 10
11.	Figure S11: BFP fitted crystal thicknesses	S11
12.	Figure S12: BFP fitted ratio of the in-plane and out-of-plane dipoles	S11
13.	Figure S13: BFP image, model and comparison without polariser	S12
14.	Figure S14: BFP in-plane [100] vs [010] dipoles ratio	S12
15.	Figure S15: TEM images and diffractions	S12
16.	Figure S16: Polarised absorption data fit on single crystal	S 13
17.	Figure S17: Polarised PL data fit on single crystal	S15
18.	Figure S18: Polarised PL maps and analysis	S16
19.	Figure S19: GW-BSE band structure and exciton calculations of $[AgSePh]_{\infty}$	S17
20.	Figure S20: The silver benzene-chalcogenides compounds family	S 18
21.	Tables S1,2,3,4: Ellipsometry fit parameters	S18
22.	Table S5: Lattice parameters used in DFT calculations	S19
23.	Table S6: Symmetry-forbidden reflections	S21



Figure S1. Steady state absorption spectrum of $[AgSePh]_{\infty}$ **.** The 1st and 2nd derivative of the spectrum clearly highlight the three excitonic resonances in the visible located at X₁ = 2.67 eV, X₂ =2.74 and X₃ = 2.86 eV, respectively.



Figure S2. Fluence dependence of the transient absorption amplitude in $[AgSePh]_{\infty}$. The data was measured at excitation energy $E_{ex} = 3.75$ eV and at t₀ (pump-probe overlap). The dashed line denotes a linear fluence dependence. Temperature 297 K.



Figure S3. Ultrafast transient absorption dynamics for varying excitation energy. Temporal dynamics of the excitonic peaks X_2 at 2.74 eV (a,c) and X_3 at 2.86 eV (b,d) for pump energies from $E_{ex} = 2.95$ eV to 3.22 eV. For $E_{ex} > 3.04$ eV and at 0 < t < 1 ps (a,b) and at 0 < t < 1.5 ps (c,d), we observe an ultrafast decay associated with the onset of free charge carrier excitation. Solid lines are fits to the data for estimating the magnitude of free carrier absorption. Pump fluence $32 \mu J/cm^2$, temperature 297 K. Temporal dynamics at high energies (c,d) suffer broadening from less compressed pump pulse due to our technical limitations. Nevertheless they clearly show increased peak amplitude due to free-carries absorption. Panel (e) shows the extended X_2 peak amplitude trend at higher excitation energies compared to the one reported in the main text (Figure 1d) to highlight the free carriers onset.



Figure S4. Atomic force microscopy of $[AgSePh]_{\infty}$ single crystals and films of the (a,b) micro-crystalline sample and the (c,d) nano-crystalline (NC) film. Measured thicknesses are 40 nm and 70 nm respectively, and the measured roughnesses (RMS) are about 3 nm for the micro crystal surface and 9 nm for the NC film.



Figure S5. Grazing-incidence wide-angle X-ray scattering (GIWAXS) 2D map of $[AgSePh]_{\infty}$ nanocrystalline (NC) film. The anisotropic intensities related to the (00X) planes with X = 2, 4, 6 are highlighted (red boxes). This shows a preferential alignment of the NCs in the film with the inorganic layers parallel to the substrate. We checked that the 2D map with Ewald sphere correction does not alter the location of the planes in the q_z direction.



Figure S6. P-XRD area detector images of the (**a**) NC film and the (**b**), micro crystalline sample, highlighting increased alignment in (**b**) of the crystal planes (00X) along the substrate. Scale bars, 5 nm⁻¹.



Figure S7. Absorption coefficient of nano-crystalline films vs. single crystals. a, Comparison of optical transmission spectrum for the NC film and the single crystal. The NC film appears to have a scattering contribution that is no longer present in the single crystal spectrum, where the absorption drops to zero around 1.7 eV. **b**, Calculated attenuation coefficient (transmission spectrum normalized by sample thickness) plotted in semi-log scale. The value of the attenuation coefficient matches at the excitonic resonances.



Figure S8. Integrated PL maps of a (**a**) NC film and a (**b**) micro-crystalline sample. The integrated PL emission intensity of the micro-crystallites is enhanced by approximately one order of magnitude compared to the NC film. The excitation power was kept constant for the two scans.



Figure S9. Schematic of the three-layer system for the back focal plane model.



Figure S10. Schematic of the optical system for back focal plane (BFP) imaging (not to scale). When the Bertrand lens is in place, the focal plane is moved from the sample (normal imaging mode) to the back focal plane of the objective, which shows the angular emission pattern.



Figure S11. Fitted crystal thicknesses from the polarised back focal images.



Figure S12. Fitted ratio of the in-plane (IP, [010] direction) to the out-of-plane (OP) dipole strength from the polarised back focal plane images.



Figure S13. BFP without polariser. a, Measured BFP image with no polariser in place. b, Modelled BFP image. c, Extracted profiles for measured and modelled BFP images at $k_x = 0$ (dark blue) and $k_y = 0$ (light blue). The dipole strength for in-plane dipoles aligned along [010] is on average 2.4x stronger than for in-plane dipoles aligned along [100].



Figure S14. BFP in-plane [010] vs [100] dipoles ratio. Fitted ratio of the dipole strengths of in-plane dipoles aligned along [010] to in-plane dipoles aligned along [100] from the unpolarised back focal plane images. The dipole strength for in-plane dipoles aligned along [010] is on average 2.4x stronger than for in-plane dipoles aligned along [100].



Figure S15. TEM image and diffraction. a, High-Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscope (STEM) image of a single crystal. The blue arrows indicate the crystal high symmetry directions [100], [010]. **b**, Single crystal electron diffraction pattern from the region marked

by the red X in (a) (the electron beam size is approximately 10 nm). The blue arrows and overlaid diamond in (b) indicate the relationship between the crystal orientation and lattice vectors. c, STEM image and electron diffraction patterns of AgSePh sample. Blue and red framed diffraction patterns are from the same single crystal domain with a beam zone-axis perpendicular to the AgSe plain at two different locations, while orange framed diffraction pattern comes from a different single crystal. Cyan and magenta squares demark the (100) and (010) reflections respectively. Very low intensity of (100) and (010) reflections indicate region with herringbone (p2gg projection symmetry, see Table S6) ordering of ligands (red framed panel) while the presence of these reflections in another part of the same crystallites indicates disorder in ligand orientations. Orange framed diffraction pattern indicates domain with p2mg like symmetry in ligand orientations, see Table S6. To summarise, TEM provides a good estimate of unit cell parameters a and b, both equal to 4.78 ± 0.15 Å, while c results to be 29 ± 1 Å, see Table S5 for comparison to the values used in theoretical calculations. On the other hand, quantitative measurement of α carries on significant error and is between 82 and 88 degrees (standard deviation > 10) and no estimate for β and γ were possible.



Figure S16. Fitting procedure for the polarised absorption spectra. **a**, For a given linear polarisation of excitation light, the absorption spectrum is acquired and fitted with three Gaussian peaks, corresponding to the three excitonic resonances (X_1, X_2, X_3) , on top of a polynomial background. The procedure is repeated rotating the light polarisation with step of 5 degrees from 0 to 360 degrees. **b**, The Gaussian peaks used for fitting plotted with colorbars representing their heights. **c**, The Gaussian peaks are then normalized in amplitude by imposing a unitary peak area, and their amplitudes are plotted versus the polarisation angle (the polar plot version is shown in the main text, Figure 4b).



Figure S17. Fitting procedure for the polarised photoluminescence (PL) spectra. **a**, For a given polarisation of the PL emission, the spectrum is acquired and fitted with 2 asymmetric peaks, corresponding to the two excitons (X_1 , X_2). The asymmetry is introduced to account for a lower energy tail, clearly visible in the X_1 exciton (panel **a**) likely arising from defect-related emission processes. The procedure is repeated rotating the polariser that filters the PL with steps of 20 degrees from 0 to 360 degrees. **b**, The Gaussian peaks used for fitting plotted with colorbars representing their heights. **c**, The Gaussian peaks were then normalized in amplitude by imposing a unitary peak area, and their amplitudes plotted versus the polarisation angle (the polar plot version is shown in the main text, Figure 4d).



-0.20-0.15-0.10-0.050.00 0.05 0.10 0.15 0.20

Figure S18. Polarised photoluminescence maps and analysis. a-b, PL maps obtained by pumping the crystals with laser (2.86 eV, pulse width 150 fs, 80 MHz repetition rate, 150 μ W average power) polarised along the maximum (a) and minimum (b) absorption of the exciton X₃ of the brightest crystal (the pump polarisation are indicated by the purple arrows, the propagation vectors are out-of-plane). c, The absorption difference caused by the pump polarisation gives rise to a different PL contrast for differently oriented crystals. The intensity map is defined as $I_c = (I_a - I_b)/(I_a + I_b)$, with being I_a and I_b the PL intensity of panel (a) and (b), respectively. d, Optical image of the pumped area. From the contrast map it is evident that the orientation of the crystals plays a major role in PL polarisation. Nevertheless, it seems that thinner crystals have higher PL anisotropy, suggesting a more disordered structure for thick crystals along the out-of-plane direction. Scale bars, 10 μ m.



Figure S19. DFT and GW band structure calculations of $[AgSePh]_{\infty}$. a, Calculated DFT(PBE) (grey) and $G_0W_0@PBE$ (blue) band structure of bulk $[AgSePh]_{\infty}$ The wavefunction distributions of the valence and conduction bands at the Γ and at the *N* points are also shown. b, Calculated GW-BSE low-lying exciton states in crystal coordinates. The table shows the excitation energies and oscillator strength; the plots show the excitons distribution at *k*-space, as explained in the main text. c, Polarization-dependent GW-BSE absorption, showing the peak dependence on the [a,b,0] in-plane light polarization direction. In this figure, the polarization directions are referenced to the primitive unit cell used for all calculations, as described in the Methods section of the main text and as detailed in Table S5.



Figure S20. The silver benzene-chalcogenides compounds family. a-b, X-ray powder diffraction indicating very similar diffraction patterns, matching the calculated structures. b, Close up view of the first diffrection peak, indicating the interlayer spacing being detuned respect to the [AgSePh]_{∞} (blue line) for the [AsSPh]_{∞} (yellow line) and the [AgTePh]_{∞} (red line). c, Visual representation of the chalcogens substitution in the crystal lattices.

Assignment	E(eV)	Amp	Br (eV)
	1.769	0.053	3.0815
X_1	2.670*	0.146	0.0688
X_2	2.740*	0.515	0.0941
X_3	2.860*	1.094	0.2120
	3.416	0.053	1.1247

Table S1. In-plane dielectric function from ellipsometry. For ellipsometric fits, the excitons are modelled as Gaussian oscillators. (*) denotes parameters that are fixed in value based on the absorption measurements.

Parameter	Value
E _{inf}	0.00
UV Pole Amp	155.4363
UV Pole En	7.902
(eV)	
IR Pole Amp	0.2463

Table S2. Further parameters for the ellipsometric model of the in-plane dielectric function.

Assignment	E(eV)	Amp	Br (eV)
	0.382	0.073	0.6360
X_1	2.670*	0.166	0.1067
X_2	2.740*	0.224	0.0807
X_3	2.860*	0.614	0.2348
	3.394	0.265	1.2639

Table S3. Out-of-plane dielectric function from ellipsometry. For ellipsometric fits, the excitons are modeled as Gaussian oscillators. (*) denotes parameters that are fixed in value based on the absorption measurements.

Parameter	Value
Einf	0.214
UV Pole Amp	295,4637
UV Pole En	9.066
(eV)	
IR Pole Amp	0.4127

Table S4. Further parameters for the ellipsometric model of the out-of-plane dielectric function.

	а	b	С	α	β	γ
Experimental cell	4.78 ± 0.15	$4.78 \pm 0.15 \text{ Å}$	29 ± 1 Å	82-88°	-	-
parameter (by TEM	Å					
diffraction),						
[primitive cell]						
Unit cell parameters	4.684 Å	4.685 Å	29.124 Å	86.373°	93.627°	77.674°
from DFT relaxation						
[primitive cell]						
Unit cell parameters	5.87607Å	7.29890 Å	29.124 Å	90°	95.7895°	90°
from literature ¹						
[conventional cell]						

The parameters of the primitive cell are related to the conventional cell by the following transformation:²

Conventional lattice	Primitive lattice
$\mathbf{a} = (a, 0, 0)$	$a_{\text{primitive}} = (a/2, b/2, 0)$
$\mathbf{b} = (0, \mathbf{b}, 0)$	$\mathbf{b}_{\text{primitive}} = (-a/2, b/2, 0)$
$\mathbf{c} = (0, c \cos \alpha, c \sin \alpha)$	$\mathbf{c}_{\text{primitive}} = (0, c \cos \alpha, c \sin \alpha)$

Where a, b, c, α , are the lattice parameters corresponding to the conventional cell.

Atomic positions (crystal units) from DFT relaxation:

	Х	У	Z
Ag1	0.11950	0.11950	0.25000
Ag2	0.88050	0.88050	0.75000
Ag3	0.51833	0.51833	0.25000
Ag4	0.48167	0.48167	0.75000
Se1	0.61069	0.02611	0.20468
Se2	0.38931	0.97389	0.79532
Se3	0.02611	0.61069	0.29532
Se4	0.97389	0.38931	0.70468
C1	0.48500	0.14200	0.14130
C2	0.51500	0.85800	0.85870
C3	0.14200	0.48500	0.35870
C4	0.85800	0.51500	0.64130
C5	0.30480	0.31340	0.04870
C6	0.69520	0.68660	0.95130
C7	0.31340	0.30480	0.45130
C8	0.68660	0.69520	0.54870
C9	0.69660	0.08340	0.10760
C10	0.30340	0.91660	0.89240
C11	0.08340	0.69660	0.39240
C12	0.91660	0.30340	0.60760
C13	0.59570	0.16430	0.05970
C14	0.40430	0.83570	0.94030
C15	0.16430	0.59570	0.44030
C16	0.83570	0.40430	0.55970
C17	0.10190	0.36410	0.08090
C18	0.89810	0.63590	0.91910
C19	0.36410	0.10190	0.41910
C20	0.63590	0.89810	0.58090
C21	0.19540	0.28860	0.12740
C22	0.80460	0.71140	0.87260
C23	0.28860	0.19540	0.37260
C24	0.71140	0.80460	0.62740
H1	0.24030	0.36190	0.01780
H2	0.75970	0.63810	0.98220
H3	0.36190	0.24030	0.48220
H4	0.63810	0.75970	0.51780
H5	0.89200	0.99800	0.11640
H6	0.10800	0.00200	0.88360
H7	0.99800	0.89200	0.38360
H8	0.00200	0.10800	0.61640
H9	0.72250	0.11770	0.03660
H10	0.27750	0.88230	0.96340
H11	0.11770	0.72250	0.46340
H12	0.88230	0.27750	0.53660
H13	0.90660	0.44780	0.07190

H14	0.09340	0.55220	0.92810
H15	0.44780	0.90660	0.42810
H16	0.55220	0.09340	0.57190
H17	0.06270	0.33650	0.14970
H18	0.93730	0.66350	0.85030
H19	0.33650	0.06270	0.35030
H20	0.66350	0.93730	0.64970

Table S5. Structural parameters of the bulk structure used in this work.

Projection symmetry	Crystal symmetry	Real space glide parallel to	Systematic absences (n = any integer)
þg	P12 ₁	b	(0 k): k = 2n + 1
cm	C12	—	(h k): h + k = 2n + 1
p2mg	P222 ₁	a	$(h \ 0): h = 2n + 1$
p2gg	P22 ₁ 2 ₁	a,b	(0 k): $k = 2n + 1$
			$(h \ 0): h = 2n + 1$
c2mm	C222	_	(h k): h + k = 2n + 1
p4gm	P4212	a,b	(0 <i>k</i>): <i>k</i> = 2n + 1
			$(h \ 0): h = 2n + 1$

Table S6. Symmetry-forbidden reflections in 2D space groups.³

Bibliography

- 1 H. L. Cuthbert, A. I. Wallbank, N. J. Taylor and J. F. Corrigan, *Z. Für Anorg. Allg. Chem.*, 2002, **628**, 2483–2488.
- 2 W. Setyawan and S. Curtarolo, Comput. Mater. Sci., 2010, 49, 299–312.
- 3 M. J. Landsberg and B. Hankamer, J. Struct. Biol., 2007, 160 3, 332–43.