Absorption Dissymmetry Factor Enhancement: A Data-Driven Approach to Unravel the Synthesis Knobs of Chiral 2D Perovskites

Raphael F. Moral,[1,2†] Maher B. Alghalayini,[2,3†] Raushan N. Nurdillayeva,[2,4] Do-Kyoung Lee,[1,2] Tim Kodalle,[2,5] Paulo E. Marchezi,[6] David P. Fenning,[6] Marcus M. Noack,[3] Craig P. Schwartz,[1] Carolin M. Sutter-Fella[2*]*

Affiliations

[1]Nevada Extreme Conditions Laboratory, University of Nevada, Las Vegas, Las Vegas, Nevada 89154, United States

[2]Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, 94720, CA, United States

[3]Applied Mathematics and Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, 94720, CA, United States

[4]Khoja Akhmet Yassawi International Kazakh-Turkish University, Turkistan, 161200, Kazakhstan

[5]Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[6] Aiiso Yufeng Li Family Department of Chemical and Nano Engineering, University of California San Diego, 9500 Gilman Drive, La Jolla, California 92093, United States.

† These authors contributed equally

*Corresponding authors:

Raphael F. Moral, rfmoral@lbl.gov

Lead contact: *Carolin M. Sutter-Fella, csutterfella@lbl.gov*

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Summary

Chiral 2D metal halide perovskites (MHPs) are promising for spin-optoelectronic applications, yet their absorption dissymmetry factor (g_{abs}) exhibits significant variability due to complex, co-dependent structural and experimental factors. We established a data-driven framework using Pearson correlation, ANOVA, and Gaussian process regression to identify and model key synthesis "knobs" governing these properties. Analysis reveals that solvent choice is the primary factor driving variability. For acetonitrile-based films, g_{abs} is maximized by optimizing annealing temperature and film thickness. Conversely, films from higher boiling point solvents show complex dependencies on annealing temperature, excitonic integral intensity, and film texture. These statistical correlations provide a roadmap for the rational design of high-performance chiral MHPs and establish a foundation for future machine-learning-driven materials exploration.

Introduction

Chirality is a geometric property of objects that are not superimposable on their mirror images, typically due to the absence of improper symmetry elements such as mirror planes, inversion centers, and rotation-reflection axes. In chemistry, molecules or crystalline materials with identical chemical composition and structure can present chirality simply due to their different spatial arrangements. Chiral semiconductors exhibit differential optical response to circularly polarized light (chiroptical properties) owing to their non-centrosymmetric structure.[1,2] These materials are relevant for new energy technologies, benefiting from the chiral-induced spin selectivity phenomenon.[2,3]

Chiral, two-dimensional (2D) metal halide perovskites (MHPs) are potential candidates for spintronics and optoelectronic devices due to their spin-polarization and chiroptical properties.[4–6] These MHPs incorporate organic cations featuring a chiral center, typically alpha NH_3^+, resulting in chirality transfer from the organic cations to the crystal structure. This chirality transfer generates spin-polarized valence and conduction bands and differential absorption of circularly polarized light, known as circular dichroism (CD).[7,8] In crystallographic terms, the material crystallizes with a chiral arrangement in one of Sohncke's non-enantiomorphic space groups, $P2_12_12_1$.[9] The mechanism of chirality transfer, likely related to N-H---X hydrogen bonding (X = Cl, Br, or I) and X-Pb-X bond angle variations within the corner-sharing octahedra, remains under debate.[7,10,11] The differential absorption of left and right circularly-polarized light is related to electric and magnetic transition dipole moments of excitonic and band-to-band transitions associated with a dissymmetry factor (g_{abs}).[12,13]

For practical applications, thin film fabrication of chiral 2D MHPs is often necessary.[14,15] However, polycrystalline thin films exhibit low chiroptical activity, associated with low g_{abs} values. The highest absolute values of g_{abs} for chiral 2D perovskites at the main excitonic peak fluctuate

around 10^{-3}, in a scale whose maximum is 2.[16] In addition, reported g_{abs} values for chiral 2D (*R-/S*-MBA)$_2$PbI$_4$ (*R-/S*-MBAPI) with the chiral organic cations *R*- and *S*-α-methylbenzylammonium vary more than two orders of magnitude for *nominally the same thin film material* (**Figure 1a**).[17–22] Some reported sources of variation include precursor concentration,[23,24] annealing temperature,[18] solvent choice,[18,22,23] deposition atmosphere,[17] and additives/impurities.[17,20] To this end, synthesis-chiroptical property correlations are lacking but are necessary to advance the field.

Here, we established synthesis-chiroptical property relationships by systematically probing experimental fabrication "knobs" of spin-coated thin films to enhance CD response (**Figure 1b)**. We combined statistical analyses, including Pearson correlation and analysis of variance (ANOVA), with Gaussian process regression (GPR) to identify the parameters that significantly influence g_{abs} and model their effects. To investigate these dependencies, we prepared *R-/S*-MBAPI thin films from single-crystal precursor solutions using acetonitrile (ACN), dimethylformamide (DMF), and a ACN:dimethyl sulfoxide (ACN:DMSO) mixture. We found that solvent choice is the main parameter affecting g_{abs}, as it modulates morphology, orientation, and optical response, with ACN films exhibiting higher g_{abs} compared to the DMF and ACN:DMSO counterparts. In films prepared with ACN, ANOVA and GPR identified film thickness (in terms of excitonic integral intensity, e_{int}) and temperature as key parameters affecting g_{abs}, whereas in those prepared with the DMF and ACN:DMSO, temperature, e_{int}, and film texture (-FWHM) were identified as the key predictors. To validate these results, *in-situ* and *ex-situ* X-ray diffraction, scanning electron microscopy (SEM), and optical measurements were performed, revealing distinct structural and optical features depending on the solvent used. In brief, our prediction of synthesis-chiroptical property relationships offers key insights for the rational design of chiral 2D MHP thin films.

Results

Chiral 2D *R-/S*-MBAPI thin films were prepared by dissolving their single crystals (SCs) in three different solvents: ACN, DMF, and 7:1 ACN:DMSO mixture. The SCs were synthesized following a previously reported method[17] adapted from the literature.[18,23] The SC solutions were spin-coated onto indium-doped tin oxide (ITO) substrates and annealed at 65°C, 100°C, or 120°C. This deposition method constitutes the main sample dataset for the statistical analysis and GPR (48 samples). In addition, dynamic thin film depositions were also carried out (see **Methods**), and their parameters were extracted (14 samples), resulting in a full dataset of 62 samples. A spreadsheet with all the considered parameters can be found in the **Supplementary Material**, and a summary of the deposition methods and film preparation conditions is given in **Table S1**. More specifically, we examined the solvent used and annealing temperature (experimental knobs), texture -FWHM (structural knobs), and excitonic peak position and integral intensity (optical knobs), **Figure 1b**.

Pearson correlation analysis and application of ANOVA and GPR

We identified complex interdependencies between the input parameters and the observed g_{abs}. We systematically quantified the relationships between these variables to understand the effect of the parameters on g_{abs}. For this, the absolute values of the dissymmetry factor ($|g_{abs}|$) were used, as g_{abs} can range between -2 and 2.[16] For each sample, we investigated multiple variables related to the fabrication knobs to serve as input parameters to ANOVA and GPR. Details on the extraction of parameters from experimental data can be found in **Methods**. We employed a multi-step statistical approach composed of Pearson correlation analysis, ANOVA, and GPR (see **Methods** section). The full dataset found in **Table S1** was not used for the statistical analysis, as comparing different deposition methods would add variability to the data that our parameters of interest cannot explain.

Pearson correlation was used to examine the linear pairwise relationships between all parameters; a critical preliminary step, as correlated variables can cause multicollinearity and unreliable results in ANOVA and GPR models. To verify that Pearson correlation (which assumes linearity) adequately characterized these relationships, Spearman rank correlation was also performed as a complementary check (see **Methods** section). Comparing Pearson (**Table S2)** and Spearman (**Table S3)** shows similar correlation values, indicating that, where relationships exist between parameters, they are linear relationships. We note that since Pearson and Spearman showed similar results, Pearson was chosen for subsequent analyses. ANOVA was then used to identify statistically significant linear effects, accounting for measurement variability and noise, and distinguishing true parameter influences from random fluctuations. While Pearson showed predominantly linear pairwise relationships, the combined effect of multiple parameters on g_{abs} may involve interactions and nonlinear response surfaces that do not appear in pairwise analysis. Hence, GPR was employed as a flexible, non-parametric approach capable of modeling complex multivariate relationships, including interaction effects and nonlinear dependencies that emerge when multiple parameters act together. GPR also provides accurate predictions of g_{abs} with uncertainty estimates even from limited datasets. Together, these methods offer a comprehensive framework for understanding both the direct and nuanced dependencies governing g_{abs}.

Pearson correlation coefficients (r) show strong g_{abs} correlation with the solvent used for film fabrication (**Table S2**, $r = 0.77$), as this can also be concluded from the box plots in **Figure 2a**. This trend splits the samples into two subsets: one for low boiling point (b.p.), ACN-based samples, and another for higher b.p., DMF/ACN:DMSO-based samples. ACN solvent yields films with overall higher g_{abs} compared to DMF and ACN:DMSO analogs.

Next, Pearson correlation analysis of the ACN subset reveals multicollinearity among several variables, as indicated by the highlighted entries in **Table S4**. Multicollinearity was defined as $|r| \geq 0.7$ between input parameters, indicating that they contain overlapping information. Temperature exhibits a high correlation with the excitonic absorption peak ($r = 0.94$) and g_{abs} ($r = 0.74$). Thus, temperature was selected as a key predictor and peak position was excluded from GPR analysis. Although e_{int} and -FWHM exhibit weak Pearson coefficients with respect to g_{abs} ($r =$

0.11 and -0.30, respectively), they were included in the GPR analysis as they may contribute to g_{abs} through interaction effects that are not captured by pairwise correlation.

GPR predictions using temperature, e_{int}, and -FWHM as inputs are displayed in **Figure S1**, with a prediction root mean square error (RMSE) of 7.8%. Sparse data points in the low-e_{int}-high-temperature region cause higher uncertainty levels. The GPR predictions show virtually no influence of -FWHM on g_{abs} in the case of ACN samples. In contrast, g_{abs} reaches its optimal values at intermediate e_{int} for all annealing temperatures, revealing a nonlinear relationship between these two parameters. Additionally, g_{abs} increases linearly with increasing annealing temperature, in line with Pearson analysis from **Table S4**, reaching its maximum value ($|g| \approx 1.4 \times 10^{-3}$) at 120°C.

To better visualize the influence of temperature and e_{int} on g_{abs}, we excluded -FWHM from the GPR modeling, resulting in the prediction surface depicted in **Figure 2b**. This new model, with an RMSE = 8%, clearly shows the trends found previously: there is an optimal g_{abs} at intermediate values of e_{int} for each annealing temperature. Again, the regions with sparse data points show the highest uncertainty (**Figure 2c**). To gain deeper insights into our modeling outputs, we conducted ANOVA using all the initial parameters chosen for GPR (**Table S5**). ANOVA confirms the statistical significance of the linear effect of temperature ($p = 0.0006 < 0.05$) and shows no statistically relevant linear effects associated with e_{int} and -FWHM, in agreement with GPR modeling (**Figure 2b** and **Figure S1**). Thus, statistical analysis of ACN-derived samples reveals consistent trends across Pearson correlation, ANOVA, and GPR, pointing to temperature and e_{int} as the main parameters affecting g_{abs}. For better visualization of the GPR plots, readers are referred to the interactive 3D images in the **Supplementary Material**.

We also analyzed the thin films made from higher b.p. solvents, namely DMF and ACN:DMSO. Pearson correlation analysis (**Table S6**) reveals pairwise correlation between -FWHM and absorption peak position ($r = 0.73$), with -FWHM having a higher correlation with g_{abs} ($r = 0.81$). Annealing temperature and e_{int} do not correlate with any other parameter and also have low Pearson coefficients with g_{abs} (r = -0.01 and -0.52, respectively). As before, e_{int} and -FWHM can have nuanced effects on the g_{abs}, and thus we performed ANOVA and GPR including -FWHM, e_{int}, and annealing temperature as predictors.

GPR modeling for DMF and ACN:DMSO samples, with RMSE = 12% (**Figure 2d**), reveals a complex interplay between predictors and g_{abs}. In this case, g_{abs} is influenced more significantly by -FWHM and e_{int}, while temperature shows a more discrete effect. To better visualize these dependencies, a GPR analysis excluding -FWHM was performed (**Figure S2**), yielding a prediction with increased RMSE (18%). **Figure S2** shows a non-negligible effect of temperature despite the increase of RMSE, reinforcing the multivariate nature of the g_{abs} prediction for DMF and ACN:DMSO samples. In addition, ANOVA results (**Table S7**) further confirm the statistical significance of all three parameters accounted for by GPR modeling in **Figure 2d**.. Uncertainty increases at high e_{int} and -FWHM values (**Figure 2e**), also due to sparse data coverage in that area, suggesting that actual g_{abs} values may be underestimated in these regions. Interestingly, the optimal

g_{abs} is also achieved at intermediate e_{int} values, similarly to ACN samples, but being affected by a more complex interplay between -FWHM and annealing temperature.

Chiral 2D *R*-/*S*-MBAPI formation, phase purity, and solvent effect

Thus far, we have not considered the phase purity of the chiral 2D MHPs, although many samples used for ANOVA and GPR have 1D phase contamination (**Table S1**). The 1D phase has (*R*-/*S*-MBA)PbI_3 stoichiometry, and it is formed by 1D pillars of face-sharing PbX_6 octahedra. The thin films exhibiting the highest g_{abs} values (**Figure S3**) show contamination with the 1D phase, which may be undesirable for practical applications, as reduced conductivity in *R*-/*S*-MBAPI has been linked to the presence of this phase.[18] To investigate the effects of solvents and temperature on film formation and phase-purity, we employed *in-situ* X-ray diffraction (XRD) during film deposition.

Temperature is decisive for phase purity, and thermal annealing below 80°C is required to achieve phase-pure chiral 2D *R*-/*S*-MBAPI thin films (**Figure 3a**). Due to the low b.p. of ACN (~82°C), the material formation with this solvent starts even before the annealing at 65°C, as evident from **Figure S4** depicting the first 350 s of film formation. On the other hand, DMF and ACN:DMSO solvents slow down the formation kinetics, with diffraction peaks of the 2D phase appearing after the beginning of the annealing (**Figure 3b-c**). This slower formation is directly related to the higher b.p. and donor number (DN)[25] of DMF and DMSO compared to ACN. The DN is a metric of the electron-donating ability of a certain Lewis base (solvent) to a Lewis acid (Pb^{2+}, in this case).[26] For instance, DMSO is known to form solution complexes with Pb^{2+}, which significantly decreases the formation kinetics of lead halide perovskites.[27,28] The DMF film maintains phase purity and stability during the 10-minute annealing at 65 °C, in agreement with the experiments with ACN solution. For ACN:DMSO, despite the initial formation of phase-pure chiral 2D MHPs (~160 s), a hydration of the film occurs subsequently (~300 s). This hydration occurs because DMSO does not fully evaporate at 65°C and absorbs atmospheric water. The formation of this hydrate phase in *R*-/*S*-MBAPI has been recently reported.[17]

To evaluate the thermal stability of *R*-/*S*-MBAPI, we increased the annealing temperature of the ACN sample every five minutes until the complete decomposition of the material (**Figure 3a**). At temperatures as low as 80°C, a slow thermal degradation initiates, leading to the appearance of the 1D phase. The degradation occurs through the thermally-induced loss of one equivalent of the MBA^0 (neutral amine) and HI, possibly facilitated in the presence of water.[17] Upon further increase in temperature, the thermal degradation is accelerated until the point where the 2D phase diffraction peaks disappear, leaving behind only the 1D material (*ca.* 2000 s in **Figure 3a**). A purely thermal degradation pathway occurs with annealing temperature ≥ 100°C even in a N_2-filled glovebox (**Figure S5**). We note that the thermal degradation observed in **Figure 3a** is intrinsic to the material, as it is completely formed and the solvent is completely dried before reaching 80°C. Although temperature control is fundamental to prevent the formation of 1D phase,

high temperature annealing is required for high g_{abs} values for ACN samples, imposing a trade-off between phase-purity and optimized g_{abs}.

The precursor solvent affects the morphology of the films significantly (**Figure 3d-f**). The resulting microstructure of the ACN film consists of a mix of small and large grains, as shown in its SEM image in **Figure 3d**. The microstructure of the DMF film is irregular, with micrometer-sized grains surrounded by a shapeless underlying layer that is not uniformly distributed across the film (**Figure 3e**). Despite the irregular morphology, the absence of diffuse scattering and sharp diffractions in **Figure 3b** suggests an entirely crystalline material. The ACN:DMSO precursor solution also results in an irregular morphology with uncovered areas between large, scale-like plates. Smaller crystallites form agglomerates in the uncovered areas, while micrometric crystals partially cover the surface of the larger plates. This complex morphology may be a result of the different evaporation rates of ACN and DMSO (DMSO b.p. = 189°C). The irregular morphology of DMF and ACN:DMSO films can be attributed to the slow and incomplete evaporation of these solvents during the 10-minute annealing at 65°C. **Figure S6** shows a complete set of SEM images for all three samples. Similarly inhomogeneous morphologies have been reported for DMF, DMSO, and N-methyl-2-pyrrolidone (NMP) films, even with high temperature annealing.[22–24]

The film texture was identified by Pearson correlation, ANOVA, and GPR, as a key structural feature of *R*-/*S*-MBAPI and is influenced by solvent choice. The breadth of peak intensity as a function of -angle reflects the distribution of crystallites with preferred orientation, where a narrower -FWHM indicates higher texture. In this context, texture refers to the ratio of crystallites oriented along the [002] lattice direction to the non-oriented ones. While all solvents promote mostly parallel slab preferential orientation, evidenced by out-of-plane (002l) diffraction peaks at $q_{xy} = 0$, they produce films with distinct texture characteristics (**Figure 4a–c**).

Films prepared with ACN appear highly textured; *i.e.*, a higher proportion of crystallites aligned parallel to the substrate (**Figure 4a**). In contrast, DMF and ACN:DMSO produce less textured films with broader -FWHM values (**Figure 4b-d**). Notably, both DMF and ACN:DMSO randomly lead to a bimodal -angle distribution, possibly indicating a roof-like arrangement of the inorganic slabs (**Figure 4e**). The morphology of ACN:DMSO films sheds light on this bimodal intensity pattern: large crystallites form adjacent tilted wedges converging at an elevated central point. In addition, overlapping of layers is observed at the junction between neighboring wedges, as illustrated in **Figure S7**.

The bimodal intensity distribution across the -angle is not consistently observed for DMF and ACN:DMSO systems and its profile varies with annealing temperature (**Figure S8a-b**). At elevated temperatures ($T \geq 100\,°C$), DMF solutions yield a broad yet homogeneous film texture, while ACN:DMSO-based films yield improved film texture as the temperature increases. In contrast, ACN-derived films maintain a consistent texture across all annealing conditions, as evidenced in the similarly narrow -FWHM values (**Figure S8c**). This variability in texture for DMF and ACN:DMSO suggests higher irreproducibility of chiral 2D MHP films fabricated with these solvents when compared to their ACN counterparts. A last remark on the structural

differences of films deposited with distinct solvents is that DMF- and ACN:DMSO-based films exhibit narrower diffraction *q*-FWHM relative to ACN (**Figure S9**); this is likely due to the presence of larger crystalline domains and a slower film formation process during deposition.

Elevated annealing temperatures promote 1D phase formation across all solvents (**Figure S8**), but the structural response varies with solvent choice. A particular feature of ACN:DMSO at 100 °C is the emergence of two distinct phases: the hydrate phase, similar to the one observed in **Figure 2c,** and an additional phase, possibly a DMSO-MBA-PbI complex, as shown in **Figure S8b** and diffraction peaks in **Figure S10**. The formation of this hypothetical DMSO-MBA-PbI phase is supported by the work of Yuan *et al.*, reporting the synthesis of a DMSO-coordinated, -methylphenethylammonium-based chiral lead bromide with similar low-*q* diffractions.[29] We link the overall lower g_{abs} values observed in **Figure 2a** for DMF and ACN:DMSO samples to these structural differences compared to ACN analogs, as the CD spectrum is highly sensitive to the morphology, texture, and impurities of thin films.[16] In addition, the presence of the hydrate phase decreases the CD response of chiral 2D MHPs.[17] The observed sensitivity of the chiroptical response to texture and morphology aligns with findings by Makhija *et al.*, who reported a similar dependence of circular dichroism on texture in 1D chiral metal halide phases.[30]

Chiroptical properties and dissymmetry factor

CD is highly sensitive to any structural or experimental changes during the formation of the chiral 2D MHPs' thin films. The reason for such sensitivity involves a complex interconnection of intrinsic and extrinsic factors, as discussed above. In the dataset excluded from ANOVA and GPR, films produced *via* dynamic deposition (see **Methods**) consistently show lower g_{abs} across all solvents (**Figure S11**), highlighting the impact of spin-coating methods on chiroptical response. Additionally, dynamic deposition yields thinner films compared to static depositions with the same precursor solution concentration (**Figure S12**). The lower g_{abs} of the dynamically deposited films sheds light on the effect of e_{int}, which is directly related to film thickness, as we discuss below in more detail. This result is aligned with GPR predictions showing that g_{abs} decreases with thinner films (*i.e.*, low e_{int} values, **Figure 2**). At last, **Figure 4f** clearly displays distinct CD and absorption spectra of *R*-/*S*-MBAPI thin films deposited with different solvents using the same deposition conditions (static + annealing at 65°C).

ACN films reproducibly showed specular differential absorption of both *R*-/*S*-MBAPI, with a g_{abs} of approximately 10^{-3} at 502 nm. In stark contrast, DMF and ACN:DMSO films displayed noisy CD signals with features at irregular positions, with g_{abs} of 1.9×10^{-4} and 3.7×10^{-4} at 504 nm and 499 nm, respectively. This distinct optical response for DMF and ACN:DMSO samples is also observed across different annealing temperatures (**Figure S13**). In addition, these samples exhibit linear dichroism (LD) and linear birefringence (LB), as shown in **Figure S14**, which also reveals irregular signals and temperature-dependent variations. The presence of LDLB in DMF and ACN:DMSO thin films is directly linked to structural anisotropies arising from the texture of the samples.[31] The occurrence of LDLB is verified by averaging the CD spectra from front and back

side of the thin film (see **Methods** for details).[16] This variability associated with different solvents is in agreement with earlier studies where CD and morphology variations were reported to be solvent-dependent.[18,22,23] Finally, we fabricated thin films using Cyrene as a chiral, non-protic, polar solvent and observed no enhancement in g_{abs} for either *S*- or *R*-MBAPI (**Figure S15**). The inability of Cyrene to improve g_{abs} confirms that solvent effects are complex and arise from changes in film morphology, texture, and/or crystallinity. This explains why some achiral solvents enhance g_{abs} (*e.g.*, ACN), while others do not (*e.g.*, DMF). A systematic study of multiple chiral solvents would be valuable but is outside the scope of this work.

Differential scattering of circularly polarized light may also influence the g_{abs} and CD spectrum. For ACN and DMF samples, the absorption before the optical bandgap is nearly zero, indicating high transmission of the films and, therefore, little influence of scattering effects. However, ACN:DMSO-based films are more opaque than ACN and DMF counterparts (**Figure S16**), and scattering effects can be observed in the baseline of the absorption spectra of ACN:DMSO samples (**Figure 4f**); this can be an additional effect lowering the g_{abs} in this case. Additional scattering effects can be visualized in **Figure S13**, with the wavelengths extending beyond 550 nm.

Discussion

The experimental features observed across solvent systems support the trends identified in our multimodal statistical analysis. ACN-based films exhibit consistent structural and optical properties, indicating that control of extrinsic factors is sufficient to optimize g_{abs}. For this purpose, GPR reveals that controlling the annealing temperature and film thickness is a key optimization strategy. The influence of temperature in ACN films can be explained in terms of residual strain. Residual strain decreases with increasing annealing temperature, consistent with prior reports on both chiral[18] and non-chiral[32] 2D MHPs (**Figure S17**). In addition, residual strain is also found to be influenced by film thickness in 2D and 3D MHP films.[32–34] Here, thickness is expressed in terms of e_{int}, as it scales linearly with the concentration of the precursor solution for film fabrication (**Figure S18**). Note, however, that g_{abs} is not linearly affected by thickness: 0.10 M precursor solutions consistently yield higher g_{abs} than 0.05 M and 0.15 M (**Figure S19**), in agreement with GPR predictions in **Figure 2**. Therefore, under optimized conditions (120°C, 0.10 M, and static deposition), ACN-based films achieved $g_{abs} > 10^{-3}$ and exhibited minimal residual strain (**Figure S3** and **Figure 2b**), aligning with findings by Scalon *et al.*[18]

In contrast, DMF and ACN:DMSO samples show less reproducible properties across external controls, resulting in irregular morphology and texture. These films consistently yield lower g_{abs} ($< 5\times10^{-4}$) and exhibit LDLB signals, reflecting the high sensitivity of CD to microstructural features and texture anisotropies. Thus, ANOVA and GPR analyses identify annealing temperature, e_{int} (thickness), and -FWHM (texture) as the dominant predictors of g_{abs} in these systems. Notably, DMF and ACN:DMSO films exhibit a broader range of -FWHM values (5° to 20°) compared to

ACN-based films (2° to 6°), making texture a critical parameter for these high-boiling-point solvents. A recent study by Hautzinger *et al.*,[34] supports this conclusion, showing that different solvents, precursors' concentration, and annealing conditions alter film texture and produce thickness variations. This thickness variation induces periodic strain modulations in the film, altering chiroptical properties and inducing additional optical effects like strain-induced birefringence. These findings align with our GPR results, which reveal a complex interplay between temperature, thickness, and texture in DMF/ACN:DMSO films. Across all solvent systems, g_{abs} exhibits a nonlinear dependence on e_{int}, reinforcing film thickness as a universal optimization parameter for *R*-/*S*-MBAPI thin films.

Circular dichroism dissymmetry factor (g_{abs}) in prototypical (*R*-/*S*-MBA)$_2$PbI$_4$ chiral 2D metal halide perovskites (MHPs) is governed by a complex interplay of intrinsic and extrinsic parameters, leading to reported values that span more than two orders of magnitude. By combining analysis of variance (ANOVA) with Gaussian process regression (GPR), we not only predicted g_{abs} trends across different solvents and film properties but also provided the most influential control parameters. Films deposited from acetonitrile precursor solutions exhibited the most reproducible structural and optical characteristics, and optimizing annealing temperature and film thickness in this system maximized g_{abs}. In contrast, dimethylformamide and acetonitrile:dimethyl sulfoxide solvent mixture produced films with irregular morphology and texture, yielding lower and less predictable g_{abs}; an effect clearly captured by the multivariate dependence of g_{abs} on annealing temperature, films thickness, and texture in both ANOVA and GPR analyses. Our comprehensive statistical framework connects film structure and optical response, providing a roadmap for rationally tuning g_{abs}. To further develop chiral 2D MHPs and improve their chiroptical properties (*e.g.*, $g_{abs} \geq 10^{-1}$), we anticipate that effective screening of the synthesis parameter space guided by active learning and machine-learning-driven closed loop experiments in combination with different chiral molecules provides an avenue forward.

Methods

Materials and Methods

S-(-)- -methylbenzylamine (98%), and R-(+)- -methylbenzylamine (98%) were purchased from Sigma Aldrich. Lead(II) oxide (99.99% metals basis) was purchased from Thermo Scientific Chemicals. Hydroiodic acid (HI, 57 wt. % in H2O, distilled, stabilized, 99.95%) was purchased from Sigma Aldrich. Acetonitrile (99.9%, gradient grade, suitable for HPLC), N,N-dimethylformamide (anhydrous, 99.8%), and dimethyl sulfoxide (suitable for HPLC, ≥ 99.7%) were purchased from Sigma Aldrich. All the chemicals were used as received. FTO and pre-patterned ITO substrates were purchased from Automatic Research GmbH and MSE Supplies, respectively.

Parameters extraction for ANOVA and GPR analysis

Experimental parameters of 48 samples were extracted in order to perform the statistical analysis (**Table S1**). The dissymmetry factor (g_{abs}) was extracted within an interval of ± 5 nm from the excitonic peak in the absorption spectra, always the largest value within this interval. The dissymmetry factor quantifies the differential absorption of left and right circularly-polarized light for a given chiroptical transition; in the case of this work, the main excitonic absorption at approximately 500 nm. From the absorption spectra measured simultaneously with circular dichroism, we extracted the excitonic peak position and excitonic integral intensity (e_{int}). **Figure S20** shows an example of how we extracted these parameters. First, we subtract a baseline from 460 to 600 nm range. Then, we integrate the peak after background subtraction to obtain the e_{int}. From the diffraction data, we extracted the -FWHM. by integrating the (002) diffraction of all samples over the -angle (or azimuthal angle, see **Figure 4a** in the main text). Then, from the plot of intensity *vs.* -angle, we fit a Voigt distribution function to the data and extracted the -FWHM.

Williamson-Hall analysis:

We used Williamson-Hall (W-H) analysis to evaluate the effect of residual strain in the lattice and crystallite size on the diffraction peak broadening and peak shift. The broadening of the diffraction due to crystallite size is given by Scherrer equation (**Eq. 1(a)**),[35] where: D is the crystallite size perpendicular to the diffraction direction, K the Scherrer constant, is the X-ray wavelength; and are the FWHM of the diffraction and the Bragg angle, respectively, both in radians. The residual strain is defined as $= d/d$, where d is the strain-free lattice spacing of the (002l) diffractions extracted from single crystal[36] data. Therefore, is a measure of d-spacing variation compared to the strain-free lattice. The relation between strain and diffraction parameters is given by **Eq. 1(b)**.[32,37] Finally, the W-H method allows for the evaluation of the contribution of both and D from parameters extracted from diffraction data. The combination of **Eq. 1(a)** and **1(b)** results in **Eq 1(c)** and **1(d)**. W-H analysis was performed according to recent reports on chiral and

non-chiral 2D MHPs.[18,32] To obtain the peak FWHM and peak positions from the (002l) diffractions, we fitted the peaks with Voigt functions. The residual strain can be obtained from the slope of the curve *cos* ( ) *vs.* [*4sin* ( )] from **Eq. 1(d).** The plots and fits are displayed in **Figure S21** in the **Supplementary Information**.

$$D = \frac{k\lambda}{\beta_D cos\theta} \qquad \text{Eq. 1(a)}$$

$$\varepsilon = \frac{\beta_\varepsilon}{4\,tan\theta} \qquad \text{Eq. 1(b)}$$

$$\beta_{hkl} = \beta_D + \beta_\varepsilon \qquad \text{Eq. 1(c)}$$

$$\beta_{hkl}\cos(\theta) = 4\,\varepsilon \sin(\theta) + \frac{K\lambda}{D} \qquad \text{Eq. 1(d)}$$

Single crystal synthesis:

This synthesis protocol is the same reported previously in more detail.[17] In a 20-mL vial, 200 mg of PbO (0.9 mmol) is dissolved in 5 mL of hydroiodic acid (Sigma, 57 wt.% in H_2O, stabilized) at 100 °C on a hot plate in a fume hood. After complete dissolution, 200 µl of *R*-, or *S*- -methylbenzylamine (1.55 mmol) dissolved in 500 µl of hypophosphorous acid (H_3PO_2) is added to the mixture dropwise. The flask is then loosely capped and stirred at 100 °C in a silicon oil bath at 1000 rpm to yield a clear yellow solution. The temperature is then decreased from 100 to 20 °C with a rate of 4 °C per hour (hotplate Torrey Pines Scientific - model HS70). After this time, roughly 1 cm long orange needles of (*R-/S*-MBA)$_2$PbI$_4$ are formed. Impure single crystals may result from fast cooling or if the solution is cold when -methylbenzylamine is added, which induces the formation of a precipitate.

The supernatant of the reaction is disposed of, and the single crystals are thoroughly washed with 50 mL of toluene; initially, they are rinsed with ~25 mL of toluene in the same reaction flask, and then transferred to a clean flask and rinsed with another 25 mL of toluene. After this step, the single crystals are washed with a mixture of 3:1 ratio of toluene and diethyl ether (total 20 mL) to remove the residues of HI. Finally, the single crystals are washed with an additional 15 mL of neat toluene (3 x 5 mL) and dried in a vacuum oven overnight at 60 °C.

Thin film preparation:

Standard deposition: unless otherwise stated, thin films were prepared with 0.15 M solutions prepared with the previously synthesized single crystals. 72 mg of (*R-/S*-MBA)$_2$PbI$_4$ (0.075 mmol) was dissolved in 500 µL of acetonitrile, DMF, or a 7:1 mixture of ACN:DMSO and allowed to stir until fully dissolved. ITO substrates were cleaned with DI water, acetone, and IPA in a sonicator

bath for at least 15 minutes with each solvent in this order. The substrates were dried with a N_2 flow and allowed to dry overnight in an oven at 60 °C. Before using them to coat the films, they were treated with UV-ozone for 30 minutes. We used 40 µL of the precursor solutions to coat the films. The spinning configuration is 10 s at 1000 rpm/500 rpm.s^{-1}, and then 30 s at 4000 rpm/1000 rpm.s^{-1}. After the spin-coat step, the films were immediately annealed at 65 °C for 10 minutes. Other experiments were performed with films prepared with different concentrations of the precursor solutions (0.05, 0.1, and 0.2 M) and different annealing temperatures (100°C and 120 °C).

Dynamic deposition: The precursor solutions were prepared as described above. In this case, the spinner starts rotating at 4000 rpm (~10 s) and the precursor solution (40 µL) is dripped onto the spinning substrate at this speed, which remains spinning for another 30 s. After the completion of this step, the films are allowed to dry at room temperature.

Dynamic, hot-cast deposition (beamline): This deposition is made in beamline 12.3.2 with the *in-situ* spin coater specially designed for *in-situ* diffraction measurements. The spinner is capable of spinning and heating at the same time, and a housing cover allows for N_2 purge while X-ray diffraction is measured through Kapton windows. For this deposition, the precursor solution was dripped onto the substrate rotating at 4000 rpm at 100 °C. The flux of N_2 was either mild (normal flow rate) or high (at the maximum flow rate).

Thin film X-ray diffraction:

XRD measurements were performed in a Bruker AXS D8-Discover X-ray Diffractometer. The source used was a Co K radiation (= 1.7902 Å). All the diffractograms were reported converting the wavelength to the more commonly used Cu K radiation (= 1.5406 Å). The measurements were carried out with a Bragg-Brentano geometry with an area detector. The initial incidence and detection angles were 5 and 15°, respectively. The whole measurement was performed with three frames, where the source and detector increased by 5°/frame each, with ending positions at 15 and 25°, respectively. Because the 2D layers present a parallel orientation to the surface of the substrate, we observe strong out-of-plane diffractions in the X-ray detector. For these measurements, we set the sample stage to oscillate in a way that the films moved 2 mm in the x and 2 mm in the y directions while measuring. This way we could have an averaged signal of a larger area of the films. The integration time for each frame was 300 s (a total of 900 s for the whole measurement).

***In-situ* XRD measurements:**

In-situ XRD measurements were carried out at the 12.3.2 microdiffraction beamline at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory in a custom-made analytical chamber, allowing for processing of the thin film and simultaneous multimodal in situ measurements.[38,39] Data was collected during spin coating of thin films and thermal annealing to follow the crystallization process on pre-patterned ITO substrates. Prior to thin film fabrication, each substrate was plasma cleaned for 10 min, placed onto the integrated spin coating puck-heater,

and secured in place by a heat transfer paste. The films were prepared via either standard or dynamic, hot-cast methods described above. In the case of dynamic deposition, a pipette tip with an internal plunger was used; this pipette is important to avoid early drip of the solution before the dispensing is triggered remotely. The incident X-ray beam was held at an incidence angle of 2° with a beam energy of 10 keV. A DECTRIS Pilatus 1 M X-ray detector was placed at an angle of 35° to the sample plane, and a sample-to-detector distance of ~236 mm was used. The scattering detector distance (SDD) was calibrated using an Al_2O_3 powder standard (NIST) prior to the experiment, and the detector position remained fixed. Additionally, before the in-situ fabrication of each sample, diffraction from the bare ITO substrate was collected. This ITO diffraction data was also used for SDD finer calibration for each sample. For all the samples, an exposure time of 0.5 s was used with a frame rate of approximately 1 s^{-1}. Data reduction and treatment were performed using the Irina[40] and Nika[41] macros for IgorPro software, and then further analyzed using pyFAI and pyGIX python packages.[42–44] The temperature of the heating puck was recorded by a pre-calibrated Raytek MI3 pyrometer.

Circular Dichroism (CD) and genuine CD (CD_{gen}) calculations:

CD measurements were carried out in a J-815 Jasco spectropolarimeter. To allow for linear dichroism and linear birefringence (LDLB) corrections, we measured the films facing the source (front), and then we flipped them to measure on the other side (back). For this correction, we used the equation $CD_{gen} = 0.5\ (CD_{front} + CD_{back})$, where CD_{gen} stands for "genuine" CD. For each CD curve, we used a window from 300 to 700 nm with steps of 1 nm. The integration time at each wavelength was 1 s, and each curve was an average of 3 measurements. To calculate the dissymmetry factor (g_{abs}), an absolute number that ranges from -2 to +2 in Absorbance Units (A.U.), we used the absorption spectra from the same instrument. The g_{abs} curves were calculated using the equation: $g_{abs} = CD_{gen}/(A*32982)$, where CD_{gen} is the differential absorption of circularly-polarized light from the CD spectrum, A is an average of the front and back absorption measurements, and 32982 is a correction factor to convert g_{abs} to A.U. (1 A.U. = 32982 mdeg).[16] By calculating g_{abs} from CD_{gen}, we accounted for LDLB contributions for all the 48 entries used in the statistical analysis.

Scanning electron microscopy:

Scanning electron microscopy (SEM) images were measured using a Zeiss Gemini Ultra-55 Analytical SEM instrument with 5 kV accelerating voltage and a magnification of 20,000 times. The films were mounted on aluminum stubs (Ted Pella, Inc.) with copper tape connected to the surface to avoid charging effects.

Statistical analysis:

Pearson correlation and analysis of variance (ANOVA) statistical analyses were performed to characterize the individual effect of each input parameter on g_{abs}. The Pearson correlation (**Table**

S2) coefficient, r, measures the strength and direction of the linear relationship between two variables, with $r = 1$ indicating perfect positive linear correlation, $r = -1$ indicating perfect negative linear correlation, and $r = 0$ indicating no linear correlation.[44] To verify that Pearson correlation adequately captured pairwise relationships, Spearman rank correlation was also performed on the full dataset (**Table S3**). Unlike Pearson, which measures linear relationships, Spearman correlation uses rank-order to detect monotonic relationships. Results showed that most correlations are consistent between both approaches (**Table S2** *vs* **Table S3**), confirming that pairwise relationships are predominantly linear. Therefore, Pearson correlation was used (**Table S4** for ACN samples and **Table S6** for DMF/ACN:DMSO samples) for the multicollinearity assessment. This analysis was performed to detect multicollinearity (high correlation) among the input parameters. Highly correlated input parameters contain overlapping information; therefore, their individual effects on g_{abs} cannot be reliably differentiated, and including both in a statistical model may not provide additional insight. In fact, multicollinearity can adversely affect the stability and interpretability of multivariate regression models. To address this, only one parameter from each highly correlated pair was included in the subsequent ANOVA and GPR.

ANOVA was employed to assess the statistical significance of the main effects of each parameter on g_{abs}, taking into account experimental variability and noise.[45] This analysis helps distinguish between true effects of the input parameters on g_{abs} and those that might arise due to random fluctuations in the data. ANOVA was performed by first fitting a linear multivariate regression model to g_{abs} as a function of the input parameters. Statistical significance for each parameter was determined by hypothesis testing. Specifically, we used a t-test to assess whether the regression coefficient for each input parameter differs significantly from zero. A significance level of 0.05 was used, meaning that input parameters with p-values less than 0.05 were considered statistically significant contributors to g_{abs}; that is, changing the value of the input parameter causes changes in g_{abs}. We performed a Type III ANOVA because our experimental design was unbalanced; the data did not have equal sample sizes for each combination of input parameters.

To ensure the validity of the ANOVA results, ANOVA assumptions, namely normality and homogeneity of variance (homoscedasticity) of residuals,[46,47] were validated. The normality assumption was assessed using the Shapiro-Wilk test,[48] while homoscedasticity was assessed using the Breusch-Pagan test[49] that examines whether the variance of residuals is constant across fitted values. For both tests, a p-value greater than 0.05 indicates that the assumptions are satisfied. Additionally, diagnostic plots, Q-Q plot (normality) and residuals *vs* fitted values (homoscedasticity), were generated to visually confirm these assumptions. **Figure S22** summarizes the results of the tests, showing that all p-values are larger than 0.05, residuals follow the theoretical normal distribution line (Q-Q plot), and residuals are randomly scattered around zero with no systematic pattern (residuals vs fitted values plot). These results validate the use of ANOVA for our datasets.

Gaussian process regression:

Gaussian process regression (GPR) was used to characterize the complex, nonlinear relationships between the input parameters and g_{abs}.[50] Using GPR, we generated predictive surfaces of the g_{abs} as a function of those parameters to better understand its trends. Based on the pairwise correlations between the input parameters, we extracted the parameters that are least correlated with each other and used them as inputs to the GPR model. Due to the strong influence of the used solvent on g_{abs}, we fitted two models, one for the ACN solvent and one for DMF/ACN:DMSO solvents. The inputs to the first model were temperature and e_{int}, while those for the second were e_{int}, -FWHM, and temperature. The parameter space for each GPR model spans the range of the respective input parameters. For ACN, this spans temperatures between 60°C and 120°C and e_{int} between 20 and 65. For DMF/ACN:DMSO, this spans e_{int} between 10 and 50, -FWHM between 1 and 22, and temperatures between 20°C and 120°C. Additional GPR models are presented in the **Supplemental Material**.

GPR was used to model the complex, nonlinear relationships between the inputs and g_{abs} for each solvent. The inputs are referred to by $x=\{x_1, x_2\} \in R^2$ for ACN and $x=\{x_1, x_2, x_3\} \in R^3$, with subscripts representing the corresponding two (ACN) and three (DMF/ACN:DMSO) input parameters. The experimentally collected g_{abs} values, referred to as y, are considered to be noisy samples of the latent function f that relates the x to g_{abs}, according to the equation $y(x)=f(x)+\epsilon(x)$, with $\epsilon(x)$ being an identically and independently distributed error. GPR was chosen since it can accurately model these complex relationships with relatively small datasets while handling the noisy data. Additionally, GPR is an interpretable machine learning model, where the model parameters, also known as the hyperparameters, provide insights into the effect of each x on g_{abs}. Specifically, we use the = 3/2 Matérn kernel function with automatic relevance determination (ARD) shown in **Eq. 2(d)** to estimate the covariance between the input points in the parameter space. Depending on the model (ACN vs DMF/ACN:DMSO), this kernel function has two/three length scales $l=\{l_1, l_2\}$ or $\{l_1, l_2, l_3\}$, one for each x, that can provide insights into the sensitivity of g_{abs} on x, with smaller values indicating higher sensitivity. This can also be observed in the GPR predictions, as larger length scales generally lead to smoother predictions. Importantly, these learned length scales complement our ANOVA findings by providing a nonlinear perspective on parameter importance. While ANOVA identifies parameters with statistically significant linear effects, the ARD kernel reveals their relative importance in the full nonlinear model, with shorter length scales indicating parameters with a stronger influence on the outcome g_{abs}. In addition to the kernel function, the GPR model requires identifying a prior mean function that represents the prior expectation of the trend as a function of x before collecting any data. Starting from an uninformed prior, it is usually chosen to be the constant function. Moreover, GPR requires defining a noise function that can be used to capture the noise in the experimental data. Assuming that the experimental noise is the same at any point in the parameter space, the constant function can also be chosen as the noise function. For more information about these functions, interested readers are

referred to references 51 and 52.[51,52] With this definition, the GPR model can be mathematically defined as

$$y(x)=f(x)+\epsilon(x), \quad \text{Eq. 2(a)}$$

$$f(x)\ \ GP(\mu(x),k(x,x')), \quad \text{Eq. 2(b)}$$

$$\mu(x)=c_1, \quad \text{Eq. 2(c)}$$

$$k(x,x')=\sigma^2{}_s\left(1+\sqrt{3}\frac{\|x-x'\|}{l}\right)\exp\left(-\sqrt{3}\frac{\|x-x'\|}{l}\right), \quad \text{Eq. 2(d)}$$

$$\epsilon(x)\ \ N(0,\sigma^2{}_n), \quad \text{Eq. 2(e)}$$

$$\sigma^2{}_n=c_2. \quad \text{Eq. 2(f)}$$

In the above equation, $\{c_1,\sigma^2{}_s,l_1,l_2,c_2\}$ represents the list of hyperparameters that need to be estimated for the GPR model to be fully defined. These are usually determined using maximum likelihood estimation.

GPR models were evaluated for their prediction performance by computing the root mean square error. Since the number of experiments for each GPR model was relatively low (13 data points for the ACN model and 21 for the DMF and ACN:DMSO model, leave-one-out cross-validation was used. Specifically, for each model, one point is removed at a time with the remaining datapoints used to fit a GPR model. Then the prediction from the model ($\hat{y}$) at the removed point is compared to the experimental g_{abs} (y). This is repeated until all points are cross-validated, then the RMSE is computed as follows

$$RMSE=\sqrt{\sum_{i=1}^{N}\frac{(y-\hat{y})^2}{N}} \quad \text{Eq. 3}$$

Resource availability

Lead Contact Further information and requests for resources should be directed to the Lead Contact, Carolin M. Sutter-Fella (csutterfella@lbl.gov).

Materials Availability: All unique reagents, specifically the *R*-/*S*-α-methylbenzylammonium lead iodide single crystals, generated in this study are available from the Lead Contact upon reasonable request. All other materials and chemicals used in this study are commercially available and detailed in the **Methods** section.

Data and Code Availability: All data generated or analyzed during this study are included in the manuscript and its **Supplementary Information**. The full data supporting the findings of this paper, including the spreadsheet containing all parameters and data points used for the statistical analysis, are deposited in Zenodo repository and are publicly available (DOI:

10.5281/zenodo.18025503). This manuscript has also been previously deposited on the preprint server ChemRxiv (https://doi.org/10.26434/chemrxiv-2025-ljpc7).

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Author contributions

R.F.M. and M.B.A. are designated as first authors. R.F.M., M.B.A., and C.M.S.-F. were responsible for **Conceptualization** of the study. R.F.M. and R.N.N. led the **Investigation**, performing thin film fabrication, CD, absorption, and XRD measurements. R.F.M. and M.B.A. executed the **Data Curation** and performed the **Formal analysis** (Pearson correlation, ANOVA, and GPR). R.N.N., D.K.L., and T.K. contributed to the **Investigation**, including synchrotron XRD measurements and data discussion. R.F.M., M.B.A., and C.M.S.-F. completed the **Writing of original draft**, while M.M.N., C.P.S., D.P.F., P.E.M., D.K.L., R.N.N., and T.K. contributed to **Writing review & editing**. **Supervision** and **Project administration** were provided by C.M.S.-F., C.P.S., M.M.N., and D.P.F. **Funding acquisition** was secured by C.M.S.-F. and C.P.S. All authors performed **Validation** of the results.

Declaration of interests

The authors declare no competing interests.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT (OpenAI) and Gemini (Google) for proofreading, text optimization, and schematic image design in this manuscript. After using this tool/service, the author reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Figures list

Figure 1. [Variability of g_{abs} values and identification of synthesis control "knobs" for chiral 2D perovskites] a) Absorption dissymmetry factor (g_{abs}) values reported in the literature from references 17-22 (black squares) and from this work (purple triangles) for chiral 2D (*R-/S*-MBA)$_2$PbI$_4$ (Only absolute values were used). **b)** Illustrations of the variables influencing g_{abs} and the tunable parameters ("knobs") for optimization: **optical** includes different excitonic peak positions and peak intensities; **chemical** includes halide composition, strength/asymmetry of hydrogen bonding, and impurities; **experimental** includes solvent choice, deposition method, and annealing temperature; and **structural** includes bond angles, orientation/texture, and film morphology.

Figure 2. [Statistical solvent screening and Gaussian process regression (GPR) modeling of g_{abs} dependencies] a) Boxplots of g_{abs} as a function of solvents evidencing the overall higher values for ACN films. **b)** GPR predictions for ACN samples computing g_{abs} with excitonic integral intensity (e_{int}) and temperature as key predicting variables and **c)** its respective uncertainty surface. **d-e)** Corresponding GPR predictions and uncertainty for DMF and ACN:DMSO films with temperature, e_{int}, and texture (-FWHM) as key predictors. Note that high uncertainty is found in regions with fewer data points.

Figure 3. [*In-situ* crystallization kinetics and microstructural morphology of (*R-/S*-MBA)$_2$PbI$_4$ films across solvent systems] *In-situ* diffraction color maps during the spin-coating process of chiral 2D (*R-/S*-MBA)$_2$PbI$_4$ MHPs with precursor solutions of different solvents (vertical dashed lines are markers for temperature change): **a)** acetonitrile (in this case, a thermal degradation experiment was conducted with a temperature ramp for ~35 minutes); **b)** dimethylformamide; and **c)** a 7:1 mixture of acetonitrile and dimethyl sulfoxide; note that for this deposition, a hydrate phase forms during the annealing process. **d-f)** Scanning electron microscopy (SEM) images of the above samples prepared in a N_2-filled glovebox with 10-minute annealing at 65°C.

Figure 4. [Structural texture, orientation, and the chiroptical response in chiral 2D MHPs] a-c) *q*-space plots of the *in-situ* XRD after the formation of the films with ACN, DMF, and ACN:DMSO solutions. These panels show the material's orientation and texture on each film. **d)** -angle integration of the (002) diffraction of each panel from the top row. The -FWHM is related to the distribution of crystallites whose [002] lattice direction is out of the plane (normal to the substrate). **e)** Schematics showing the inorganic slabs of chiral 2D (*R-*/S-MBA)$_2$PbI$_4$ MHPs in stack and roof-like arrangements; ACN solution reproducibly yields stacked textures while DMF and ACN:DMSO can generate both arrangements. **f)** Circular dichroism (CD) spectra (top) for (*R-/S*-MBA)$_2$PbI$_4$ thin films deposited with different solvents and their respective absorption spectra (bottom). All the films were prepared with a 0.15 M single-crystal precursor solution and annealed at 65°C.