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Chiroptical properties of membrane glycerophospholipids and their chiral backbones

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Abstract

Glycerophospholipid membranes are one of the key cellular components. Still, their species-dependent composition and homochirality remain an elusive subject. In the context of the astrophysical circularly polarized light scenario likely involved in the generation of a chiral bias in meteoritic amino and sugar acids in space, and consequently in the origin of life's homochirality on Earth, this study reports the first measurements of circular dichroism and anisotropy spectra of a selection of glycerophospholipids, their chiral backbones and their analogs. The rather low asymmetry in the interaction of UV/VUV circularly polarized light with *sn*-glycerol-1/3-phosphate indicates that chiral photons would have been unlikely to directly induce symmetry breaking to membrane lipids. In contrast, the anisotropy spectra of *D*-3-phosphoglyceric acid and *D*-glyceraldehyde-3-phosphate unveil up to 20 and 100 times higher maximum anisotropy factor values, respectively. This first experimental report, targeted on investigating the origins of phospholipid symmetry breaking, opens up new avenues of research to explore alternative mechanisms leading to membrane lipid homochirality, while providing important clues for the search for chiral biosignatures of extant and/or extinct life in space, in particular for the ExoMars 2028 mission.

KEYWORDS

anisotropy spectroscopy, chirality, circular dichroism, circularly polarized light, lipids

1 | INTRODUCTION

Homochirality of life is one of the most fascinating unresolved scientific questions. While almost exclusive preference for *L*-amino acids in proteins and *D*-sugars in nucleic acids has received considerable attention,¹ it has somehow been left behind that glycerophospholipids (GPLs)–predominant components of membranes–are also chiral.

Remarkably, homochirality of membrane glycerophospholipids is species dependent. While in general bacterial and eukaryal membrane GPLs are fatty acid esters linked to *sn*-glycerol-3-phosphate (G3P), archaeal phospholipids are built on the backbone of the opposite handedness, that is, *sn*-glycerol-1-phosphate (G1P), and contain ether-linked isoprenoid derivatives, which if chiral are present in the *R*-configuration.² Interestingly,

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the *R*-stereochemistry motifs in branched hydrocarbons are also ubiquitous in bacteria and eukarya; notably, they are found in chlorophylls and tocopherols of cyanobacteria, algae, and higher plants, as well as in steroids, carotenoids, and ubiquinones,^{3–5} which indicates their common origins.

Despite the fundamental importance of single-molecular chirality in all biopolymers, a significant issue remains unexplored experimentally, namely, how a common asymmetric selection process for all chiral biological monomers emerged at the dawn of molecular evolution. One of the most promising hypotheses explaining the symmetry breaking of amino acids and sugars is the so-called *astrophysical circularly polarized light (CPL) scenario*.⁶ Enantiomers of chiral amino acids and sugars and/or their precursors in space would have interacted selectively with UV CPL from nearby stars, inducing a chiral bias prior to their delivery to the early Earth,^{7,8} where the initial excess would have been amplified to homochirality.⁹ In support are multiple detections of enantiomerically enriched L-amino^{1,10} and D-sugar acids^{1,11} in meteorites. Moreover, infrared CPL has been detected in the Orion¹² and NGC 6334V¹³ star-forming regions, and it is considered to extend into the UV spectral region, the detection of which is hampered by extensive extinction by dust particles. In addition, monochromatic UV CPL irradiation of racemic amino acids^{14–17} as well as achiral inter-/circumstellar ice analogs^{18,19} has been shown to lead to the molecular asymmetry in amino acids with an enantiomeric excess (*ee*) of up to about 5%.²⁰

The differential absorption of CPL by enantiomers of chiral molecules, so-called circular dichroism (CD), underlies the asymmetric photochemistry likely driving the induction of the chiral bias in space. The efficiency of asymmetric photolysis and thence the *ee* that can be induced in such reactions relates to the anisotropy factor *g* as first derived by Kagan et al,²¹ and later²² simplified as follows

$$|\%ee| \geq \left(1 - \left(1 - \frac{|g|}{2}\right)^2\right) \times 100\% \quad (1)$$

where ξ is the extent of reaction and *g* is defined as the ratio of differential absorption (CD) to the absorption of unpolarized light, and the sign of *ee* follows the sign of *g*.

In this study, we unveil for the first time the electronic CD and anisotropy spectra of the chiral backbone of glycerophospholipids, namely, *sn*-glycerol-1/3-phosphate, and their carboxylic acid and aldehyde analogs. Given the large diversity of GPLs in nature, we have selectively chosen representative bacterial/eukaryal

glycerophospholipids that span major classes based on their headgroups. These include phosphatidylcholines (PCs), phosphoethanolamines (PEs), phosphatidylserines (PSs), and phosphatidylglycerol (PG), as well as an archaeal lipid having two branched hydrocarbon (phytane) side chains (Figure 1). Our investigation into the chiroptical properties of lipids and their potential precursor molecules aims in determining whether there exists a shared origin for biomolecular homochirality in amino acids and lipids through asymmetric photochemical processes. Given the complexity of contemporary phospholipids, it is widely discussed that these appeared later in the evolution.^{23–25} However, it is entirely plausible that their precursors have extraterrestrial origins. Notably, glycerol-phosphate²⁶ and long-chain carboxylic acids²⁷ were previously detected in interstellar ice analogs exposed to galactic cosmic ray proxies. Additionally, chiral hydrocarbon side chains of archaeal phospholipids, such as phytane, pristane, and norpristane, have been found in carbonaceous chondrites.²⁸ Furthermore, ethanolamine—the simplest glycerophospholipid amino alcohol motif headgroup—was recently detected in space.²⁹

Even though complex glycerophospholipids have not been identified in any extraterrestrial material thus far, the detection of their precursors is a significant advancement in this research avenue and offers important insights for targeting lipids as chiral biomarkers in the quest for past and/or present life in space. In particular, lipids have been selected as one of the key molecules to be searched for as part of the ExoMars 2028 mission to Mars due to their great longevity over geological time-scales, which is at least an order of magnitude longer than that of RNA/DNA, proteins, or amino acids' *ee*.^{30,31}

2 | MATERIAL AND METHODS

Enantiopure standards of *sn*-glycerol-1/3-phosphate lithium salt, D-glyceraldehyde-3-phosphate solution (8–13 g L⁻¹), D-3-phosphoglyceric acid disodium salt, L- α -phosphatidylcholine from egg yolk, 1-oleoyl-2-palmitoyl-/1-palmitoyl-2-oleoyl-/1,2-dimyristoyl-*sn*-glycerol-3-phosphocholine, 1-palmitoyl-2-oleoyl-/1,2-dioleoyl-*sn*-glycerol-3-phosphoethanolamine, 1-palmitoyl-2-oleoyl-/1,2-dioleoyl-*sn*-glycerol-3-[phospho-L-serine] sodium salt, 1-palmitoyl-2-oleoyl-*sn*-glycerol-3-[phospho-*rac*-1-glycerol], and 1,2-di-*O*-phytanyl-*sn*-glycerol were purchased from Sigma-Aldrich or Avanti Polar Lipids and were used without further purification. For the liquid-phase measurements, the standard solutions in hexafluoro-2-propanol (HFIP) or deionized, filtered, and UV-irradiated ultrapure water were prepared at concentrations between

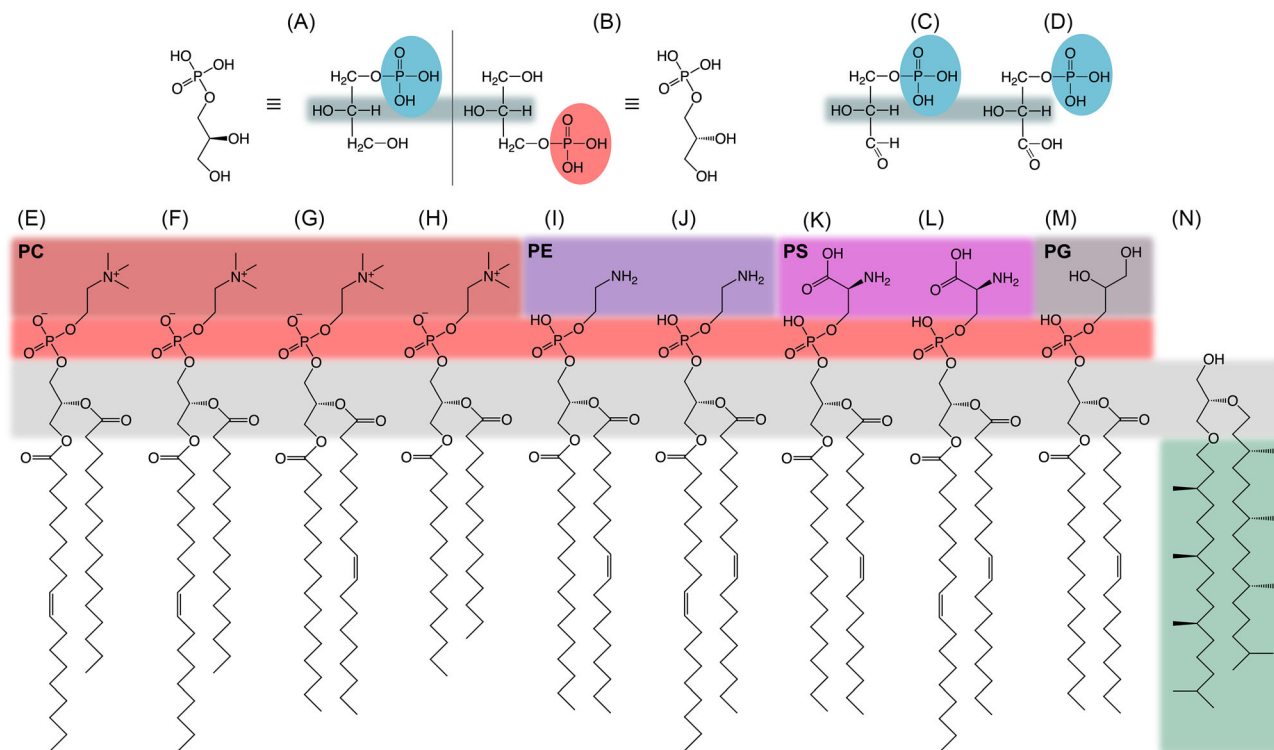


FIGURE 1 Schematic structures of chiral membrane phospholipids, their glycerol backbones, and derivatives investigated in the present study: PC, phosphatidylcholine; PE, phosphatidylethanolamine; PS, phosphatidylserine; PG, Phosphatidylglycerol. (A) *sn*-Glycerol-1-phosphate, (B) *sn*-glycerol-3-phosphate, (C) *D*-glyceraldehyde-3-phosphate, (D) *D*-3-phosphoglyceric acid, (E) *L*- α -phosphatidylcholine (lecithin) from egg yolk; lecithin is a mixture of phosphatidylcholines of varying hydrocarbon chain lengths, and the structure shown above is representative of the predominant fatty acids in lecithin from egg yolk, that is, 18:1 (*cis*-9-oleic acid) and 16:0 (palmitic acid), (F) 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine, (G) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine, (H) 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine, (I) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphoethanolamine, (J) 1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine, (K) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-*L*-serine, (L) 1,2-dioleoyl-*sn*-glycero-3-[phospho-*L*-serine], (M) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-[phospho-*rac*-1-glycerol], and (N) 1,2-di-*O*-phytanyl-*sn*-glycerol. Blue and red in (A) and (B) signify phosphate group in *sn*-1 and *sn*-3 positions, respectively. In (C) and (D), the Fischer projection for *sn*-glycero convention is maintained (OH group on C2 on the left, highlighted in dark gray) to aid comparison with (A). In (E)–(M), the phosphate group in red signifies its *sn*-3 position as in (A), which is typical of bacteria and eukarya. Dark red, purple, magenta, and dark gray stand for choline, ethanolamine, serine, and *rac*-1-glycerol headgroups. Light gray highlights the glycerol backbone. In (N), green highlights the branched hydrocarbon side chains typical of archaea as opposed to straight fatty acid tails in (E)–(M) characteristic of bacteria and eukarya.

3 and 100 g L⁻¹. For solid-state measurements on G1P and G3P lithium salts, thin isotropic films, approximately several hundred nanometers in thickness, were prepared by drop-casting 5 g L⁻¹ methanol: water (2:3 and 1:1, respectively; methanol $\geq 99.8\%$, AnalaR NORMAPUR[®] ACS) solutions of the standards onto VUV grade CaF₂ windows (Crystran), which were preheated at 60°C. The application of heat facilitated rapid solvent evaporation and ensured a uniform distribution of transparent films of G1P and G3P within the central ~ 5 mm diameter of the window. This was achieved using a custom-built heating system comprised of an aluminum block sandwiched between two Peltier elements. The temperature was set with PID regulation and monitored with a K-type thermocouple.

Electronic CD and anisotropy spectra of the standard solutions and films were recorded in the 170–250 nm and 130–300 nm wavelength range, respectively, using the AU-CD beam line of the ASTRID2 synchrotron storage ring facility, Aarhus University, Denmark. The experimental setup is described in detail in literature.^{32,33} The simultaneous measurement of differential absorption and absorption spectra was done as reported in Evans et al.³⁴ Quartz cells of nominal pathlengths of 5, 10, 20, 100, and 500 μ m were used for the measurements on the solutions. The pathlength of the 100 μ m cell was carefully measured beforehand using an interference technique,³⁵ and spectra recorded using other pathlengths were scaled according to the absorbance of the magnitude of the 100 μ m cell spectrum. The chiroptical spectra of the

solutions were examined at different concentrations to ensure good signal-to-noise ratios in the whole measured wavelength range.

To investigate the potential impact of linear dichroism and linear birefringence from sample alignment on the solid-state CD spectra of G1P and G3P, we recorded the CD signals at several rotations (at 0° , 90° , 180° , and 270°) around the axis of the incident synchrotron radiation normal to the sample surface and ensured that the changes were small. The final CD spectrum is the average of all rotated spectra ensuring that the spectrum is free from possible alignment artefacts. Measurements of the cleaned CaF_2 windows were performed with the same rotations to remove contributions from the windows and other components of the spectroscopic setup. Additionally, to confirm the positions of zero-crossings, extrema, and g values, thin films of *sn*-glycerol-1- and *sn*-glycerol-3-phosphate were repeatedly prepared and utilized for recording the anisotropy spectra. We took meticulous care to produce optically transparent films, ensuring their thickness was kept sufficiently thin to prevent any adverse effects of scattering, while also taking care that films were uniform to avoid effects from absorbance flattening. All spectra in this study were recorded with a 2 s

dwell time, wavelength steps of 1 nm, and multiple accumulations per enantiomer. A mild 7-point window Savitzky–Golay filter smoothing was applied to the CD spectra and consequently also to the resulting anisotropy spectra.

3 | RESULTS AND DISCUSSION

Figure 2 displays the CD and anisotropy spectra of *sn*-glycerol-1/3-phosphate—the chiral backbone of glycerophospholipids—in aqueous solution and in the isotropic solid phase. The spectra of the enantiomeric pair in both states (Figure 2A,C) show quasi-perfect mirror symmetry with similar band positions and magnitudes, confirming the reliability of the recorded data. The aqueous solution CD and anisotropy signals of both enantiomers are characterized by a dominant band with the extrema at ~ 172 nm and ~ 179 nm ($g_{179} \approx 0.0003$ for G1P), respectively. Comparison with previously measured CD and anisotropy spectra of various straight-chain secondary alcohols and diols in aqueous solution shows striking similarity. All these spectra exhibit a strong dichroic peak at about 180 nm, attributed to the

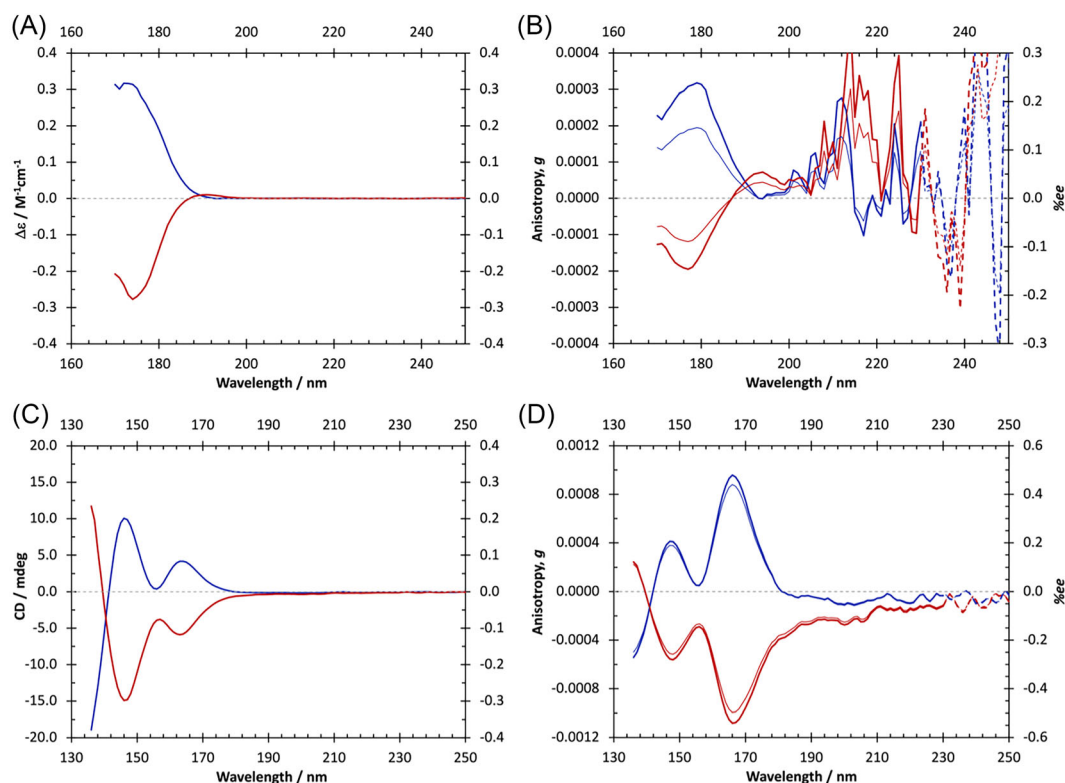
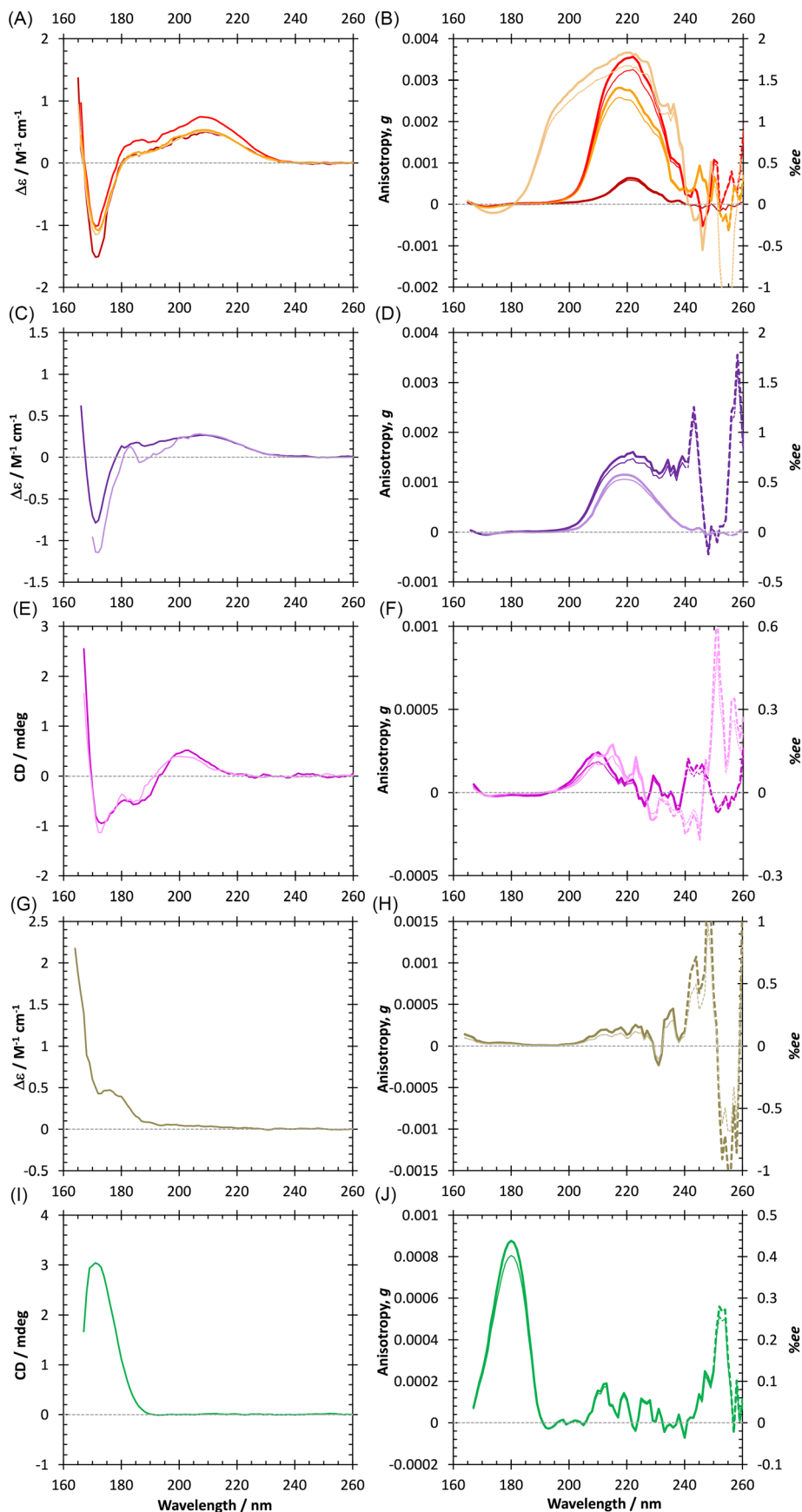


FIGURE 2 Chiroptical properties of *sn*-glycerol-1/3-phosphate (blue/red) reveal their small enantioselective sensitivity to circularly polarized light. (A,C) Electronic circular dichroism and (B,D) anisotropy spectra (thick lines) of G1P/G3P lithium salt in aqueous solution and in the solid phase, respectively. The ee inducible by asymmetric photolysis by monochromatic circularly polarized light at the extent of reaction $\xi = 0.9999$ is indicated by thin lines in (C) and (D).

FIGURE 3 Chiroptical properties of representatives of glycerophospholipids with choline, ethanolamine, serine, and *rac*-1-glycerol headgroups as well as of a dialkylated glycerol with *R*-configurations on the side chains in hexafluoro-2-propanol (HFIP). Left figures are CD spectra, while on the right are the anisotropy g (left hand scale) and associated enantiomeric excess (ee) calculated with an extent of reaction $\xi = 0.9999$ (right hand scale). (A,B) *L*- α -Phosphatidylcholine (dark red), 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (red), 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (orange), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (light orange), (C,D) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphoethanolamine (dark purple), 1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine (light purple), (E,F) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-*L*-serine sodium salt (dark magenta), 1,2-dioleoyl-*sn*-glycero-3-[phospho-*L*-serine] sodium salt (light magenta), (G,H) 1-palmitoyl-2-oleoyl-*sn*-glycero-3-[phospho-*rac*-1-glycerol], and (I,J) 1,2-di-*O*-phytanyl-*sn*-glycerol. The ee inducible by asymmetric photolysis by monochromatic circularly polarized light at the extent of reaction $\xi = 0.9999$ is indicated by thin lines in (B,D,F,H) and (J). Due to the poor solubility of some samples, and thence unknown concentrations of the respective solutions, we do not report the molar ellipticity in (E) and (I).



$n \rightarrow \sigma_{\text{CO}^*}$ transition, along with anisotropy values of about $g \approx 0.001$, except for 2,3-butanediol, which displayed a markedly increased anisotropy factor of $g \approx 0.009$.³³ As a reference, the longer wavelength region of the anisotropy spectra is depicted with thin dashed lines throughout the manuscript, as the errors resulting from the low intensity of the absorbance and CD signals are too pronounced to ascertain reliable g values.

In the absence of an aqueous solvation shell, this band shows a hypsochromic shift to ~ 163 nm in the CD (Figure 2C) and ~ 166 nm in the anisotropy spectra ($g_{166} \approx 0.001$; Figure 2D), with about a three times higher anisotropy factor value at the extremum compared with the aqueous solution. The second, more intense, CD band is fully resolved in the solid-state CD spectrum with an extremum at ~ 146 nm and at ~ 147 nm in the anisotropy spectrum ($g_{147} \approx 0.0004$ for G1P), where the intensity is lower compared with the longer wavelength band due to higher absorption. The underlying transitions responsible for the two measured chiroptical bands are yet to be determined. In aqueous solution, this CD signal is cut off by strong absorption of water.

The anisotropy factors for G1P/G3P lithium salt are both rather small in the solid state and aqueous solution, with maximum ee inducible in an asymmetric photolysis at the extent of reaction $\xi = 0.9999$ (thin lines in Figure 2B,D) below 0.5%. Upon astrophysical conditions, stellar radiation is broadband and only partially polarized, and thence the induced ee would be even smaller. In addition, a racemic pool of *sn*-glycerol-1/3-phosphate likely synthesized on the early Earth would further

diminish the overall enantiomer enrichment delivered from space to the prebiotic *milieu*. Similarly, negligible are the anisotropy factors of the complex glycerophospholipids reported in Figure 3. The favorable solubility of representative lipids from the PC (Figure 3A), PE (Figure 3C), and PG (Figure 3G) classes facilitated the derivation and expression of $\Delta\epsilon$ in [$\text{M}^{-1} \text{cm}^{-1}$]. However, the limited solubility of PS (Figure 3E) and archaeal-type lipids (Figure 3I) posed challenges in this regard. For these lipids, each dataset was measured on saturated solutions with a pathlength of 0.1 mm.

The obvious disparity in anisotropy observed in *L*- α -phosphatidylcholine (Figure 3B, dark red), as opposed to the other investigated lipids from the same PC lipid class, could potentially be attributed to sample contamination. This inference is supported by the notably different absorbance of this particular PC lipid at longer wavelengths.

It is clear from Figure 3A,C that within the same glycerophospholipid family, slight changes in the hydrocarbon side chains' length/degree of unsaturation (Figure 1E–L) do not significantly affect the CD spectra as they do not possess a strong chromophore or an additional chiral center. On the contrary, the effect of the headgroups on the CD spectra is more apparent. While phosphatidylcholines and phosphatidylethanolamines bear great similarity in their headgroups (Figure 1E–J) and hence their CD spectra resemble each other very well (Figure 3A,C), the presence of an additional chromophore and chiral center in phosphatidylserines (Figure 3E) results in the appearance of an additional

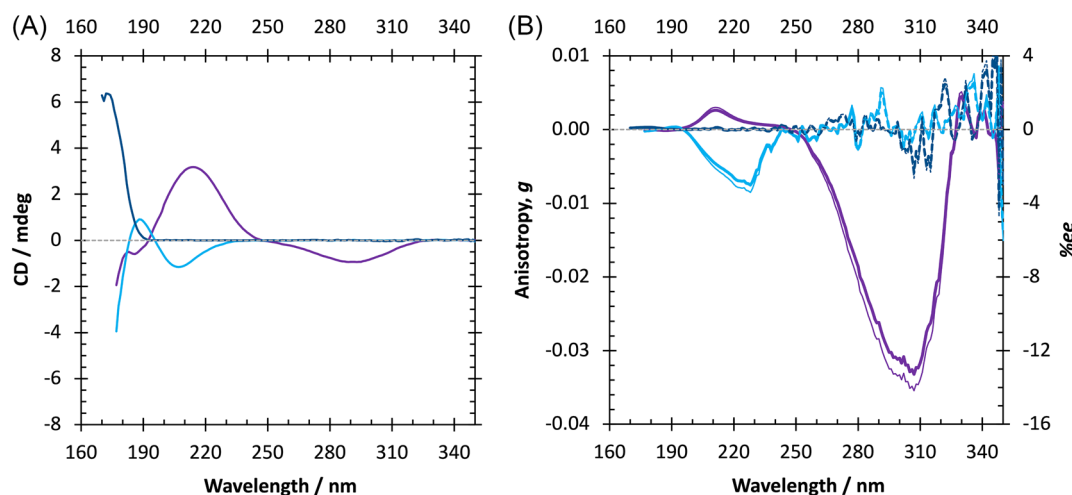


FIGURE 4 Comparison of the chiroptical properties of aqueous solutions of *sn*-glycerol-1-phosphate lithium salt = *D*-glycerol-3-phosphate lithium salt (dark blue), *D*-3-phosphoglyceric acid disodium salt (light blue, pH 5–5.5), and *D*-glyceraldehyde-3-phosphate (purple) reveals about 20- and 100-fold increase in the maximum anisotropy signal between the alcohol and acid derivatives, and between the alcohol and aldehyde derivatives, respectively. (A) Electronic circular dichroism and (B) anisotropy spectra (thick lines) and the ee inducible by asymmetric photolysis by monochromatic circularly polarized light at the extent of reaction $\xi = 0.9999$ (thin lines), respectively.

prominent negative CD band at ~ 186 nm. A sign inversion is observed for the phosphatidylglycerol lipid in Figure 3G. Analogously low anisotropy values are shown also for *R*-branched hydrocarbons ether bound to the glycerol backbone in Figure 3J, which is a characteristic motif for archaeal phospholipids. Therefore, unlike for amino acids, the direct transfer of chirality from stellar CPL to phospholipid backbone/phospholipids seems rather unlikely. This, however, also increases the likelihood that significant *ee* values in *sn*-glycerol-1/3-phosphate and/or phospholipids, if detected in space, could be indicative of a biological origin rather than abiotically generated through interaction with stellar CPL.

Interestingly, replacing the first carbon with a hydroxy group in G3P by a carboxyl ($-\text{COOH}$) or an aldehyde ($-\text{CHO}$) group leads to enhanced anisotropy values at longer wavelengths (g extrema of ~ -0.008 at 228 nm and ~ -0.033 at 307 nm, respectively; Figure 4), highlighting possible pathways for indirect chirality transfer to G1P/G3P backbones, which are to be explored. It should be noted that the chiroptical properties of D -3-phosphoglyceric acid in Figure 4 are expected to be affected by complexation with sodium ions present in the standard, as we previously reported for glyceric acid in the presence of calcium ions.³⁶ Consequently, we expect the maximum anisotropy factor of pure D -3-phosphoglyceric acid to be even higher. Importantly, for the majority of stars, the UV photon flux is expected to drop in the far UV wavelength range (<177 nm),^{12,37} and most of the UV light <200 nm is expected to be absorbed by water molecules in water-dominated interstellar ices,³⁸ which further emphasizes the advantage of long wavelength range g bands of the carboxylic acid and aldehyde derivatives as opposed to the alcohol.

4 | CONCLUSION

CD and anisotropy spectroscopy are established tools for the characterization of enantioselectivity triggered by circularly polarized light, the latter providing a direct measure of the efficiency of asymmetric photolysis. UV CPL has proven capable of inducing a chiral excess of a few % to amino acids. However, rather low anisotropy values of *sn*-glycerol-1/3-phosphate in aqueous solution, that is, mimicking an aqueous solvation shell in water-dominated interstellar ices, and likewise low values in the solid state, that is, mimicking recondensation on bare interstellar grains, both point to the inefficient generation of chiral bias via direct asymmetric photolysis into the chiral backbones of phospholipids. Although there is no strict minimum requirement for the g factor in achieving symmetry breaking through circularly polarized photons,

the relatively modest g values associated with *sn*-glycerol-1/3-phosphate, in combination with the low polarization rate of stellar UV CPL in space (maximum 20%), highlight a potential limitation. In the absence of efficient chiral amplification, this combination results in *%ee* values that predominantly fall well below 1% in the *astrophysical circularly polarized light scenario*. Such small *%ee* values not only pose challenges for common detection methods in extraterrestrial sample analyses, but they might be too subtle to drive significant chiral selection under prebiotic conditions.

In contrast, up to 20 and 100 times higher maximum anisotropy values were found for carboxylic acid and aldehyde analogs of *sn*-glycerol-1-phosphate, respectively. This suggests alternative mechanisms operating at the origins of membrane lipid homochirality that are yet to be identified. These findings are critically important for narrowing down the focus of enantioselective analyses of extraterrestrial samples and classifying biosignatures as biotic or abiotic.

AUTHOR CONTRIBUTIONS

Jana Bocková: Writing—original draft; writing—review and editing; formal analysis; visualization; investigation.

Adrien D. Garcia: Investigation; writing—review and editing.

Nykola C. Jones: Methodology; investigation; formal analysis; writing—review and editing; data curation.

Søren V. Hoffmann: Investigation; writing—review and editing; resources; funding acquisition; methodology; data curation.

Cornelia Meinert: Writing—original draft; funding acquisition; resources; conceptualization; methodology; investigation; supervision; writing—review and editing; formal analysis; data curation; project administration.

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DATA AVAILABILITY STATEMENT

All data analyzed during this study are included in this published article. The datasets generated or analyzed during the current study are available from the corresponding author upon request.

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REFERENCES

- Glavin DP, Burton AS, Elsila JE, Aponte JC, Dworkin JP. The search for chiral asymmetry as a potential biosignature in our solar system. *Chem Rev.* 2020;120(11):4660-4689. doi:10.1021/acs.chemrev.9b00474
- Peretó J, López-García P, Moreira D. Ancestral lipid biosynthesis and early membrane evolution. *Trends Biochem Sci.* 2004;29(9):469-477. doi:10.1016/j.tibs.2004.07.002
- Kates M, Joo CN, Palameta B, Shier T. Absolute stereochemical configuration of phytanyl (dihydrophytyl) groups in lipids of halobacterium cutirubrum*. *Biochemistry.* 1967;6(11):3329-3338. doi:10.1021/bi00863a001
- Leseigneur G, Filippi JJ, Baldovini N, Meierhenrich U. Absolute configuration of aliphatic hydrocarbon enantiomers identified by gas chromatography: theorized application for isoprenoid alkanes and the search of molecular biosignatures on Mars. *Symmetry.* 2022;14(2):326. doi:10.3390/sym14020326
- Caforio A, Driessen AJM. Archaeal phospholipids: structural properties and biosynthesis. *Biochim Biophys Acta - Mol Cell Biol Lipids.* 2017;1862(11):1325-1339. doi:10.1016/j.bbalip.2016.12.006
- Garcia AD, Meinert C, Sugahara H, Jones NC, Hoffmann SV, Meierhenrich UJ. The astrophysical formation of asymmetric molecules and the emergence of a chiral bias. *Life.* 2019;9(1):29. doi:10.3390/life9010029
- Oró J. Comets and the formation of biochemical compounds on the primitive earth. *Nature.* 1961;190(4774):389-390. doi:10.1038/190389a0
- Chyba CF, Thomas PJ, Brookshaw L, Sagan C. Cometary delivery of organic molecules to the early earth. *Science.* 1990;249(4967):366-373. doi:10.1126/science.11538074
- Bonner WA. The origin and amplification of biomolecular chirality. *Orig Life Evol Biosph.* 1991;21(2):59-111. doi:10.1007/BF01809580
- Cronin JR, Pizzarello S. Enantiomeric excesses in meteoritic amino acids. *Science.* 1997;275(5302):951-955. doi:10.1126/science.275.5302.951
- Cooper G, Rios AC. Enantiomer excesses of rare and common sugar derivatives in carbonaceous meteorites. *Proc Natl Acad Sci U S A.* 2016;113(24):E3322-E3331. doi:10.1073/pnas.1603030113
- Bailey J, Chrysostomou A, Hough JH, et al. Circular polarization in star-formation regions: implications for biomolecular homochirality. *Science.* 1998;281(5377):672-674. doi:10.1126/science.281.5377.672
- Kwon J, Tamura M, Lucas PW, et al. Near-infrared circular polarization images of NGC 6334-V. *Astrophys J Lett.* 2013;765(1):L6. doi:10.1088/2041-8205/765/1/L6
- Meinert C, Hoffmann SV, Cassam-Chenaï P, et al. Photone-energy-controlled symmetry breaking with circularly polarized light. *Angew Chem Int Ed.* 2014;53(1):210-214. doi:10.1002/anie.201307855
- Meierhenrich UJ, Nahon L, Alcaraz C, et al. Asymmetric vacuum UV photolysis of the amino acid leucine in the solid state. *Angew Chem Int Ed.* 2005;44(35):5630-5634. doi:10.1002/anie.200501311
- Flores JJ, Bonner WA, Massey GA. Asymmetric photolysis of (RS)-leucine with circularly polarized ultraviolet light. *J Am Chem Soc.* 1977;99(11):3622-3625. doi:10.1021/ja00453a018
- Bocková J, Jones NC, Topin J, Hoffmann SV, Meinert C. Uncovering the chiral bias of meteoritic isovaline through asymmetric photochemistry. *Nat Commun.* 2023;14(1):3381. doi:10.1038/s41467-023-39177-y
- De Marcellus P, Meinert C, Nuevo M, et al. Non-racemic amino acid production by ultraviolet irradiation of achiral interstellar ice analogs with circularly polarized light. *Astrophys J Lett.* 2011;727(2):L27. doi:10.1088/2041-8205/727/2/L27
- Modica P, Meinert C, De Marcellus P, Nahon L, Meierhenrich UJ, D'Hendecourt LLS. Enantiomeric excesses induced in amino acids by ultraviolet circularly polarized light irradiation of extraterrestrial ice analogs: a possible source of asymmetry for prebiotic chemistry. *ApJ.* 2014;788(1):79. doi:10.1088/0004-637X/788/1/79
- Meierhenrich UJ, Filippi JJ, Meinert C, Hoffmann SV, Bredehöft JH, Nahon L. Photolysis of rac-leucine with circularly polarized synchrotron radiation. *Chem Biodivers.* 2010;7(6):1651-1659. doi:10.1002/cbdv.200900311
- Balavoine G, Moradpour A, Kagan HB. Preparation of chiral compounds with high optical purity by irradiation with circularly polarized light, a model reaction for the prebiotic generation of optical activity. *J Am Chem Soc.* 1974;96(16):5152-5158. doi:10.1021/ja00823a023
- Meinert C, Bredehöft JH, Filippi JJ, et al. Anisotropy spectra of amino acids. *Angew Chem Int Ed.* 2012;51(18):4484-4487. doi:10.1002/anie.201108997
- Pohorille A, Deamer D. Self-assembly and function of primitive cell membranes. *Res Microbiol.* 2009;160(7):449-456. doi:10.1016/j.resmic.2009.06.004
- Namani T, Ruf RJ, Arsano I, Hu R, Wesdemiotis C, Sahai N. Novel chimeric amino acid-fatty alcohol ester amphiphiles self-assemble into stable primitive membranes in diverse geological settings. *Astrobiology.* 2023;23(3):327-343. doi:10.1089/ast.2022.0056
- Suzuki N, Itabashi Y. Possible roles of amphiphilic molecules in the origin of biological homochirality. *Symmetry.* 2019;11(8):966. doi:10.3390/sym11080966
- Zhu C, Turner AM, Abplanalp MJ, et al. An interstellar synthesis of glycerol phosphates. *ApJ.* 2020;899(1):L3. doi:10.3847/2041-8213/aba744
- Zhu C, Turner AM, Abplanalp MJ, Kaiser RI. Formation and high-order carboxylic acids (RCOOH) in interstellar analogous ices of carbon dioxide (CO₂) and methane (CH₄). *Astrophys J Suppl Ser.* 2018;234(1):15. doi:10.3847/1538-4365/aa9f28
- Kissin YV. Hydrocarbon components in carbonaceous meteorites. *Geochim Cosmochim Acta.* 2003;67(9):1723-1735. doi:10.1016/S0016-7037(02)00982-1
- Rivilla VM, Jiménez-Serra I, Martín-Pintado J, et al. Discovery in space of ethanolamine, the simplest phospholipid head group. *Proc Natl Acad Sci U S A.* 2021;118(22):e2101314118. doi:10.1073/pnas.2101314118

30. Wilhelm MB, Ricco AJ, Buckner DK, et al. Extraction instruments to enable detection of origin-diagnostic lipids for life detection. In: *52nd Lunar and Planetary Science Conference*. 2021; 2548: 2634.
31. Finkel PL, Carrizo D, Parro V, Sánchez-García L. An overview of lipid biomarkers in terrestrial extreme environments with relevance for mars exploration. *Astrobiology*. 2023;23(5):563-604. doi:10.1089/ast.2022.0083
32. Bredehöft JH, Jones NCJ, Meinert C, Evans AC, Hoffmann SV, Meierhenrich U. Understanding photochirogenesis: solvent effects on circular dichroism and anisotropy spectroscopy. *Chirality*. 2014;26(8):373-378. doi:10.1002/chir.22329
33. Meinert C, Jones NC, Hoffmann SV, Meierhenrich UJ. Anisotropy spectroscopy of chiral alcohols, amines, and monocarboxylic acids: implications for the analyses of extraterrestrial samples. *J Photochem Photobiol A Chem*. 2016;331:130-137. doi:10.1016/j.jphotochem.2015.12.018
34. Evans AC, Meinert C, Bredehöft JH, et al. Anisotropy spectra for enantiomeric differentiation of biomolecular building blocks. In: Schurig V, ed. *Topics in Current Chemistry*. Vol. 341. Springer-Verlag; 2013:271-299.
35. Hoffmann SV, Fanø M, van de Weert M. Circular dichroism spectroscopy for structural characterization of proteins. In: Müllertz A, Perrie Y, Rades T, eds. *Analytical Techniques in the Pharmaceutical Sciences*. Springer; 2016:223-251. doi:10.1007/978-1-4939-4029-5_6
36. Bocková J, Jones NC, Leyva V, Gaysinski M, Hoffmann SV, Meinert C. Concentration and pH effect on the electronic circular dichroism and anisotropy spectra of aqueous solutions of glyceric acid calcium salt. *Chirality*. 2022;34(2):245-252. doi:10.1002/chir.23407
37. Bianchi L, Conti A, Shiao B. The ultraviolet sky: an overview from the GALEX surveys. *Adv Sp Res*. 2014;53(6):900-912. doi:10.1016/j.asr.2013.07.045
38. Bocková J, Jones NC, Meierhenrich UJ, Hoffmann SV, Meinert C. Chiroptical activity of hydroxycarboxylic acids with implications for the origin of biological homochirality. *Commun Chem*. 2021;4(1):86. doi:10.1038/s42004-021-00524-z

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