

# Negative Nonlinear CD–ee Dependence in Polycrystalline BINOL Thin Films

Kevin Liang, Florian Ristow, Kevin Li, Johannes Pittrich, Natalie Fehn, Lukas Dörringer, Ueli Heiz, Reinhard Kienberger, Gennaro Pescitelli, Hristo Iglev,\* and Aras Kartouzian\*



Cite This: *J. Am. Chem. Soc.* 2023, 145, 27933–27938



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**ABSTRACT:** Generally, the relationship between the observed circular dichroism and the enantiomeric excess in chiral systems (CD–ee dependence) is linear. While positive nonlinear behavior has often been reported in the past, examples of negative nonlinear (NN) behavior in CD–ee dependence are rare and not well understood. Here, we present a strong NN CD–ee dependence within polycrystalline thin films of BINOL by using second-harmonic-generation circular dichroism (SHG-CD) and commercial CD spectroscopy studies. Theoretical calculations, microscopy, and FTIR studies are employed to further clarify the underlying cause of this observation. This behavior is attributed to the changing supramolecular chirality of the system. Systems exhibiting NN CD–ee dependence hold promise for highly accurate enantiomeric excess characterization, which is essential for the refinement of enantio-separating and -purifying processes in pharmaceuticals, asymmetric catalysis, and chiral sensing. Our findings suggest that a whole class of single-species systems, i.e., racemate crystals, might possess NN CD–ee dependence and thus provide us a vast playground to better understand and exploit this phenomenon.

Ranging from the characterization of enantiomeric compositions<sup>1</sup> to sensorics<sup>2</sup> and optoelectronics,<sup>3,4</sup> the demand for understanding and the application of chirality continues to increase.<sup>5</sup> Examples of the importance of chirality in energy conservation and efficient conversion include low energy consumption and large memory density devices and electronics using chiral perovskites<sup>6–8</sup> and chirality transfer to transition metal complexes for the application of asymmetric catalysis.<sup>9–12</sup> The most common manifestation of optical activity in a system is its circular dichroism (CD),<sup>13–23</sup> the preferential absorption of one circular polarization (CP) of light over the other.

There is a steady demand for improvement of enantio-separating and -enriching processes not only motivated by the pharmaceutical industry.<sup>24–26</sup> Chiroptical spectroscopic techniques provide a simple, quick, and nondestructive way to determine optical activity. However, without a clear understanding of the relation between the obtained CD and the enantiomeric excess (CD–ee dependence), this information is of little value. CD–ee dependence is most commonly a simple linear relationship but can also deviate in a positive nonlinear (PN) or a negative nonlinear (NN) manner (see SI).<sup>27–30</sup> Currently we have a good understanding of PN CD–ee dependence based on models such as the van Gestel model,<sup>31,32</sup> employing helicity reversal penalty and mismatch penalty, or the mass-balance model introduced by Markvoort and co-workers to explain the phenomenon.<sup>33,34</sup> NN CD–ee dependence, on the other hand, is rarely reported and accordingly is not well-understood. Recently a racemate rule effect (RRE) was suggested as a phenomenological description of this behavior.<sup>35</sup> The RRE is rooted in the “favored heterochirality” in the system, an idea that has found some evidence beyond catalytic applications, in the literature.<sup>27,28</sup>

The majority of chiral crystalline substances are racemate compounds, meaning that as a racemic mixture they prefer forming racemic crystals over conglomerates of enantiopure crystals.<sup>36</sup> In other words, crystals of racemate compounds favor heterochiral interactions, and thus it can be hypothesized that according to the RRE crystalline films of racemate compounds should show NN CD–ee dependence. One commonly used and well-understood racemate compound is BINOL (1,1'-bi-2-naphthol), making it a suitable model system to test the above hypothesis.<sup>20,37–43</sup>

We investigate CD–ee dependence in polycrystalline thin films of BINOL fabricated by evaporating BINOL molecules onto glass under ultra-high-vacuum conditions. We also employ SHG-CD (second-harmonic-generation CD), which provides a magnification of chiroptical effects.<sup>38,44–48</sup> FTIR experiments are also performed to provide a link between the CD–ee dependence and the molecular structure of the samples, while microscopy is used to monitor the change in the supramolecular structure with an ee at the ~100 μm scale. With the help of theoretical calculations on the energetics of the crystals, a clear understanding of the observations can be obtained.

In the following, we use the *g*-value instead of CD as the measure of optical activity, as it is normalized with respect to concentration and path-length and is generally defined as

**Received:** November 2, 2023

**Revised:** December 8, 2023

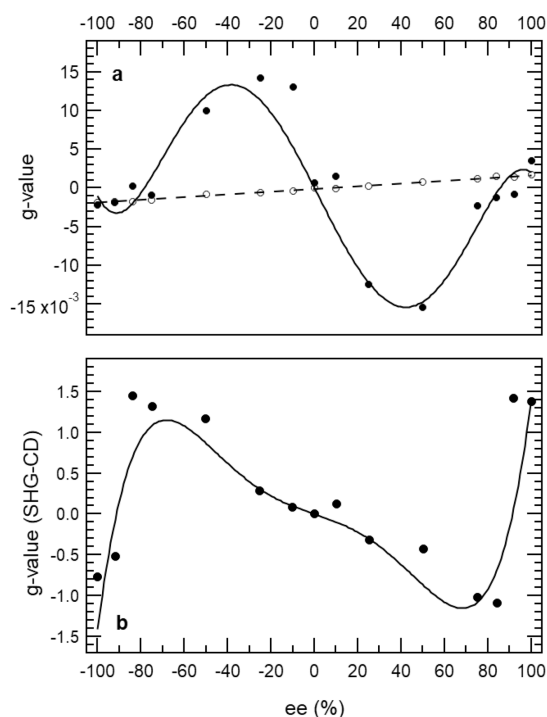
**Accepted:** December 11, 2023

**Published:** December 13, 2023



$$g = \frac{2(I_{\text{LCP}} - I_{\text{RCP}})}{I_{\text{LCP}} + I_{\text{RCP}}} \quad (1)$$

where  $I_{\text{LCP}}$  and  $I_{\text{RCP}}$  refer either to the light intensity that is absorbed by the sample with left CP and right CP light, respectively, for CD measurements performed with commercial instruments or to the SHG light intensity generated by the sample with each CP light. However, any  $g$ -value versus  $ee$  relationships will still be referred to as CD- $ee$  dependence to be compatible with previous literature. The CD- $ee$  dependence in polycrystalline BINOL films at 310 nm, close to the  $^1L_b$  transition,<sup>49</sup> presented in Figure 1a, is extracted from  $g$ -value



**Figure 1.**  $g$ -value vs  $ee$  (a) for polycrystalline BINOL thin films (solid circles, solid line) and for BINOL in solution (open circles, dashed line) at 310 nm and (b) for BINOL thin films measured by SHG-CD (bottom panel) at 310 nm (at a fundamental wavelength of 620 nm).

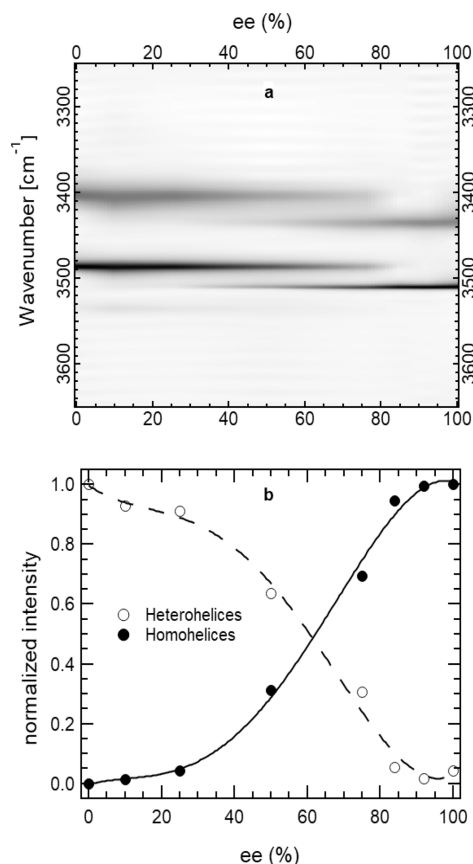
curves of the samples after considering and removal of all known nontrue-CD contributions<sup>20,50–53</sup> (see SI). The data clearly show a nonlinear CD- $ee$  dependence with a zero-crossing around 80%  $ee$ . Also shown is the CD- $ee$  dependence of solutions of BINOL in ethanol (20 mg/L of a BINOL mixture in ethanol), which shows a linear CD- $ee$  dependence as expected. We intuitively assign this difference between the two curves to the CD that originates from the structure of the thin film samples. Optical activity of the films can be understood as a superposition of the molecular contribution from individual BINOL molecules in the films and a supramolecular contribution that is due to the chiral crystals.<sup>54,55</sup> This agrees with the fact that the highest  $g$ -value does not belong to the enantiopure samples but to mixtures with ~50%  $ee$ , showing a remarkable 7-fold higher  $g$ -value. Independent confirmation is delivered by SHG-CD, which not only provides us with much higher chiroptical sensitivity<sup>38,44–47</sup> but also can be used to disentangle different contributions to the optical activity, as it is intrinsically free from nontrue-CD<sup>41</sup> (see SI). CD- $ee$  dependence of

polycrystalline BINOL films at 310 nm measured by SHG-CD is presented in Figure 1b. Here again a clear nonlinear relationship is observed, with a zero-crossing in  $g$ -value between 84%  $ee$  and 92%  $ee$ . The CD- $ee$  dependences presented in Figure 1a and 1b both clearly indicate negative nonlinear behavior, as indicated by a zero-crossing at  $ee$  values other than zero.

After having established the NN CD- $ee$  dependence in BINOL films, we attempted to describe this observation. According to Chen and co-workers, NN CD- $ee$  can be explained as the tendency of the building blocks, either single molecules or aggregates, to favor heterochiral interactions over homochiral interactions. Consequently, in such systems, racemates will be more readily formed compared to conglomerates, and thus the effect was coined “racemate rule effect”.<sup>35</sup> To relate our findings to the currently available phenomenological theory, we try to explain the observed NN CD- $ee$  dependence in terms of favorable interactions between heterochiral units in the BINOL crystals. We know that enantiopure BINOL forms crystals with  $3_1$  homochiral helices, while racemic BINOL forms crystals with a pack of  $2_1$  homochiral helices of opposite enantiomers. In both cases all BINOL molecules within each helix are of the same handedness, and thus all interactions between them are of homochiral nature.<sup>42</sup> This seems to defy the stated requirement put in place by the RRE. However, a closer look at the unit cell of the racemic crystal reveals that it requires the alternative packing of homochiral  $2_1$  helices, which appropriately can be labeled as heterohelices, whereas the homochiral  $3_1$  helices in the enantiopure crystals are logically labeled as homohelices. Accordingly, the observed NN CD- $ee$  dependence in BINOL crystals can indeed be related to the favored heterochiral interaction between neighboring  $2_1$  helices of the racemic crystal. Within this interpretation, the addition of relatively small amounts of the opposite enantiomer forces the crystal structure to change its units from  $3_1$  helices to  $2_1$  helices. Since both helices are fully homochiral, no large rearrangements are required and the molecules can keep their neighbors within each helix. The preference for the neighboring helix, however, becomes clearly heterochiral.

IR signature of hydrogen bonding between neighboring BINOL molecules for solid state BINOL can be used as an indicator of the structure.<sup>42,56,57</sup> In FTIR spectra of the racemic structure a donor/acceptor pair is observed for OH absorption at 3405 and 3486  $\text{cm}^{-1}$ , respectively, and for the enantiopure structure these bands are around 3435 and 3510  $\text{cm}^{-1}$ , respectively.<sup>42</sup> We will refer to the hydrogen bonding in the racemic structure as belonging to heterohelices to indicate the heterochiral preference of the  $2_1$  helices in the unit cell and the hydrogen bonding in the enantiopure structure as belonging to homohelices in contrast.

Since FTIR does not distinguish between the enantiomers, Figure 2 only depicts the data for  $ee$  between 0% and 100%. Figure 2a indicates that although there is a range of  $ee$  for which both peak pairs are observed, the OH absorption behaves in a binary fashion being in either one or the other state without any gradual frequency shifts in between. Figure 2b summarizes the share of hetero- and homohelices in percent as calculated by taking the ratio of the peak height at 3486  $\text{cm}^{-1}$  relative to the racemic case and the ratio of the peak height at 3510  $\text{cm}^{-1}$  relative to the enantiopure sample, respectively (see SI). In terms of relative share, a shift from homohelices to heterohelices can be observed with decreasing

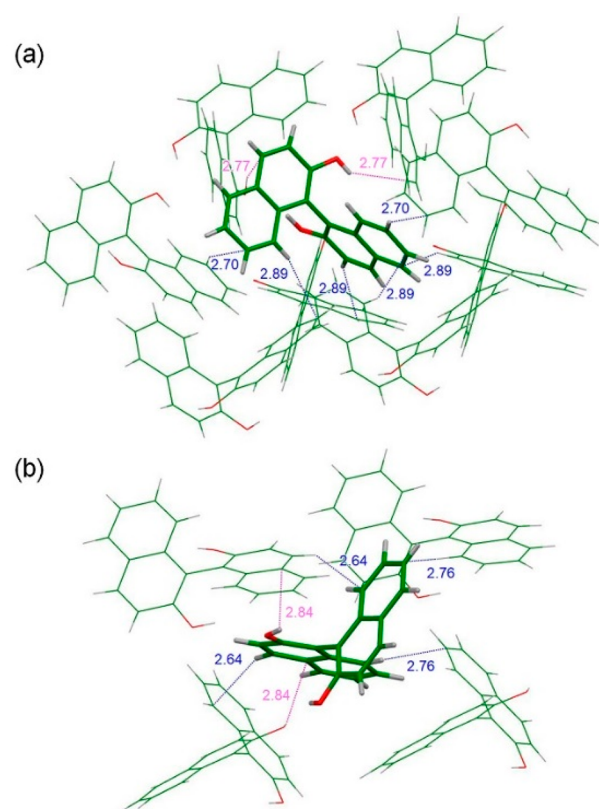


**Figure 2.** (a) FTIR peak intensities for OH absorption specific to the racemic crystal structure (heterohelices) at 3405 and 3486  $\text{cm}^{-1}$  and for the enantiopure crystal structure (homohelices) at 3435 and 3510  $\text{cm}^{-1}$ . (b) The normalized share of OH intensities for the bands at 3486 and 3510  $\text{cm}^{-1}$ .

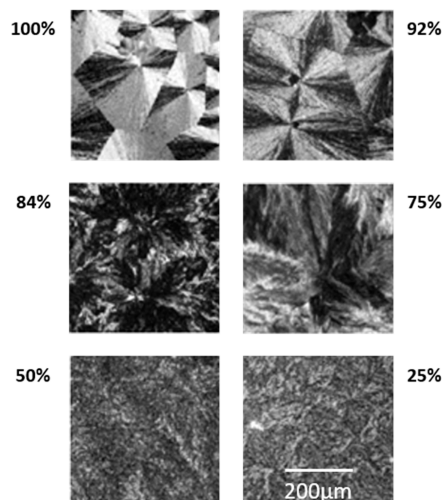
ee starting at +84% ee. We thus concluded that the NN CD–ee dependence of the BINOL thin films is related to the change in the nature of the crystal structure as indicated by the OH peak position since a zero-crossing in the CD–ee curve is observed also in the same ee range.

Inspection of the racemic and enantiopure crystals of BINOL reveals that not only hydrogen bonds but other noncovalent interactions also contribute to the stabilization of the  $2_1$  and  $3_1$  helices (Figure 3), respectively.<sup>42</sup> In the racemic compound, each BINOL unit is involved in eight short-range interactions, two of  $\text{OH}\cdots\pi$  type and six of  $\text{CH}\cdots\pi$  type, of which four with the homochiral and four with the heterochiral species. In the enantiopure compound, each BINOL unit is involved in six interactions, two of  $\text{OH}\cdots\pi$  type and four of  $\text{CH}\cdots\pi$  type. Apart from the net difference in the number of interactions, DFT calculations on all distinguishable first-neighbor dimers, namely, two for  $2_1$  helices and four for  $3_1$  helices, find an overall energetic preference of 1.6 kcal/mol for the racemate architecture (see SI). The latter also has fewer/smaller voids than the enantiopure crystal, which is in accord with higher density for the racemic compound.<sup>42</sup>

Microscopy images shown in Figure 4 also confirm the relationship between the change in the crystal structure and the CD–ee dependence of the films. Obvious differences in structure between the pure enantiomers, with larger crystal domains, compared with samples closer to the 0% ee, with smaller and finer crystal domains, are observed. The dramatic



**Figure 3.** Short intermolecular contacts measured (in Å) on the X-ray structures of the racemic (a) and enantiopure (b) BINOL. Pink:  $\text{OH}\cdots\pi$  interaction; blue:  $\text{CH}\cdots\pi$  interaction.



**Figure 4.** Cross-polarization micrographs of the thin film samples of BINOL of different ee's.

change in structure that starts at 75% ee and completes at 84% ee on the way to the enantiopure structure is distinctly different from the smooth transition at lower ee's. This behavior aligns with the change in  $g$ -value, found in Figure 1, and is also compatible with the findings of Figure 2.

Both PN and NN CD–ee dependences are highly desired for chiral-sensing applications. In PN systems, the slope of the CD–ee curve is steeper than that of the linear CD–ee curve close to 0% ee, and thus a smaller change in ee translates into a larger change in CD, providing a higher sensitivity for ee



measurement at low ee. For NN the same is true at high ee values. While many systems with PN CD–ee have been reported, systems exhibiting NN CD–ee are very scarce.<sup>28</sup> In this study, BINOL thin films of different enantiomeric excesses were investigated and identified to exhibit an NN CD–ee dependence. SHG-CD, along with CD, were used to demonstrate the presence of supramolecular contributions within the optical activity of a seemingly simple single-species chiral system. This work unambiguously demonstrates the dominant role supramolecular chirality can play in the case of polycrystalline thin films of chiral molecules. This is further supported by microscopy images, which followed the change in the supramolecular structure with ee and the structural dependence of the optical activity, as indicated by the share of OH bonds belonging to the structure that favors the proximity of heterohelices. Additionally, theoretical calculations reveal that the favored heterochirality has its origin in the better packing of the structure and higher coordination number of each BINOL molecule in the racemate structure, which is a common property of racemate compounds. These results suggest that other racemate compounds might also possess NN CD–ee dependence in the polycrystalline film state, providing us with a large number of easily available systems to investigate and thus paving the way to a deeper understanding of NN CD–ee. Most importantly, the fact that for this system showing NN CD–ee a much higher *g*-value can be obtained at an ee of ~50% compared to the enantiopure films will be of great benefit to all applications demanding material with high optical activities, e.g., chiral photovoltaics, chiral sensors, and spintronics.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c12253>.

Experimental procedures, sample preparation, extinction, CD spectra, FTIR spectra, and details of the calculations (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Aras Kartouzian** – Catalysis Research Center and School of Natural Sciences, Chair of Physical Chemistry, Technische Universität München, 85748 Garching, Germany; [orcid.org/0000-0002-2193-2902](https://orcid.org/0000-0002-2193-2902); Email: [aras.kartouzian@mytum.de](mailto:aras.kartouzian@mytum.de)

**Hristo Iglev** – Physik-Department E11 and School of Natural Sciences, Technische Universität München, 85748 Garching, Germany; [orcid.org/0000-0001-9208-0068](https://orcid.org/0000-0001-9208-0068); Email: [hristo.iglev@tum.de](mailto:hristo.iglev@tum.de)

### Authors

**Kevin Liang** – Catalysis Research Center and School of Natural Sciences, Chair of Physical Chemistry, Technische Universität München, 85748 Garching, Germany

**Florian Ristow** – Physik-Department E11 and School of Natural Sciences, Technische Universität München, 85748 Garching, Germany

**Kevin Li** – Catalysis Research Center and School of Natural Sciences, Chair of Physical Chemistry, Technische Universität München, 85748 Garching, Germany

**Johannes Pittrich** – Physik-Department E11 and School of Natural Sciences, Technische Universität München, 85748 Garching, Germany

**Natalie Fehn** – Catalysis Research Center and School of Natural Sciences, Chair of Physical Chemistry, Technische Universität München, 85748 Garching, Germany

**Lukas Dörringer** – Physik-Department E11 and School of Natural Sciences, Technische Universität München, 85748 Garching, Germany

**Ueli Heiz** – Catalysis Research Center and School of Natural Sciences, Chair of Physical Chemistry, Technische Universität München, 85748 Garching, Germany; [orcid.org/0000-0002-9403-1486](https://orcid.org/0000-0002-9403-1486)

**Reinhard Kienberger** – Physik-Department E11 and School of Natural Sciences, Technische Universität München, 85748 Garching, Germany

**Gennaro Pescitelli** – Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56124 Pisa, Italy; [orcid.org/0000-0002-0869-5076](https://orcid.org/0000-0002-0869-5076)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.3c12253>

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We acknowledge financial support by DFG through the projects KA 4166/2-3 and KI 1304/8-3 and via the Cluster of Excellence (e-conversion EXC 2089/1-390776260). N.F. thanks Studienstiftung des Deutschen Volkes.

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