

# Perfect Polar Alignment of Parallel Beloamphiphile Layers: Improved Structural Design Bias Realized in Ferroelectric Crystals of the Novel “Methoxyphenyl Series of Acetophenone Azines”



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Invited for the cover of this issue are Harmeet Bhoday, Nathan Knotts, and Rainer Glaser at the Missouri University of Science and Technology. Joe Miner, the university mascot, is a silent and honorary co-author and personifies the spirit of the old west and *the determination to succeed* (our emphasis). The image depicts one (MeO-Ph, Y)-azine molecule and a model of a perfectly polar stacked bilayer. The floodlight illumination presents a graphic metaphor of second-harmonic generation (frequency doubling) by the crystalline ferroelectric materials. Read the full text of the article at 10.1002/chem.202400182.

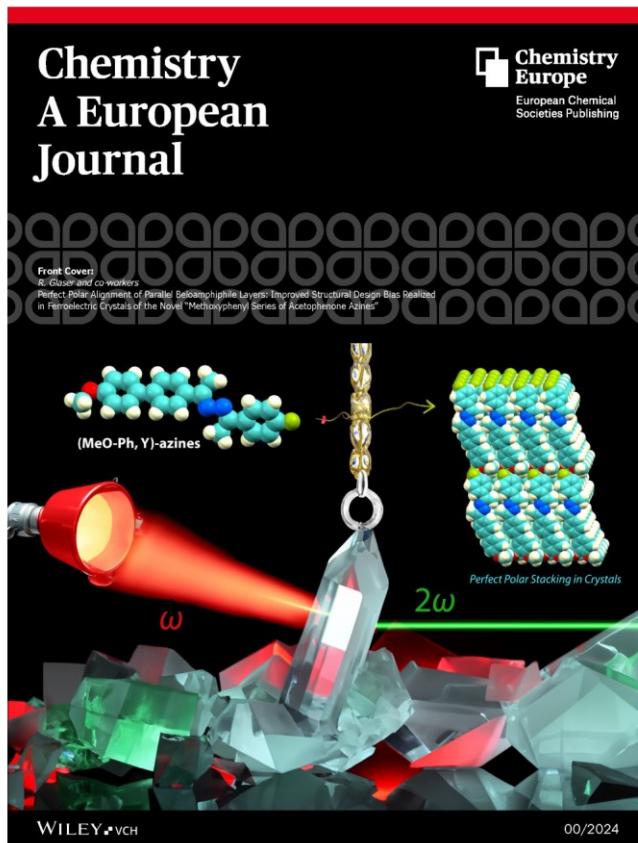
### What is the most significant result of this study?

The focal point of our research has been the design and realization of polar crystalline solids of pure molecular materials for nonlinear optics (NLO). Rather than merely seeking non-centrosymmetric crystals, we desired to design donor–acceptor-substituted organics and dipeptides that would want to crystallize with very highly dipole–parallel aligned supramolecular architectures. At the very beginning, many thought achieving this goal was impossible. Early successes were scarce and came slowly. Gradual improvements in the chromophore design and a growing understanding of supramolecular architectures and intermolecular bonding eventually led to predictable designs. With the availability of several representatives of several series of ferroelectric organics, it is now possible to establish for the very first time experimental structure–function relationships for the NLO activity of ferroelectric molecular crystals. The development of such ferroelectrics will have to go hand in hand with the refinement of software for the calculation of crystal lattice energies. While all our azine ferroelectrics are based on PBAMs, we are also exploring other supramolecular concepts to realize highly dipole-aligned molecular materials.

### What aspects of this project do you find most exciting?

The interplay between *intralayer* and *interlayer* intermolecular interactions is challenging, and finding the right balance is permanently on our mind and the subject of extensive

exciting insights about *intra-* and *interlayer* interactions.



The replacement of the methoxy- or phenoxy-substituted acetophenone,  $\text{RO}_{\text{para}}\text{Ph}(\text{Me})\text{C}=\text{O}$  by the methoxy-substituted 4-acetyl biphenyl,  $\text{MeO}_{\text{para}}\text{PhPh}(\text{Me})\text{C}=\text{O}$  drastically changes the first-order hyperpolarizability,  $\beta_0$ , of the free molecule. The  $\beta_0$  values of the free ( $\text{MeO-Ph}$ ,  $\text{Y}$ )-azines are essentially doubled compared to those of the ( $\text{MeO}$ ,  $\text{Y}$ )- and ( $\text{PhO}$ ,  $\text{Y}$ )-azines and thrice the value of the industry standard *p*-nitroaniline (PNA). Interestingly, the calculations show that the constraints on conformations imposed by the crystal structures greatly reinforce the optical performance of the materials. Whereas the free ( $\text{MeO-Ph}$ ,  $\text{Y}$ )-molecules feature twisted biphenyls, the crystals of the ( $\text{MeO-Ph}$ ,  $\text{Y}$ )-azines feature planar biphenyls that allow extended conjugation and cause an additional boost of the  $\beta_0$  values.

It is one highlight of this study that the crystals of the ( $\text{MeO-Ph}$ ,  $\text{F}$ )-azine **1** feature *perfectly* stacked PBAMs, whereas the stacking in the crystals of ( $\text{MeO-Ph}$ ,  $\text{Y}$ )-azines with  $\text{Y}=\text{Cl}$  (**2**),  $\text{Br}$  (**3**), and  $\text{I}$  (**4**) occurs with the formation of "kinks". Interlayer halogen bonding is responsible for the kinks of **2–4** because this mode of PBAM stacking ensures proper directionality of the  $\text{C}\cdots\text{Y}\cdots\text{O}$  interaction. The perfect PBAM stacking in the fluoroazine **1** crystal is made possible by the absence of  $\text{O}\cdots\text{F}$  halogen contacts and is fully compatible with the optimization of the unique  $\text{F}\cdots\text{H}_{\text{MeO}}$  bonding motif.

**What was the biggest surprise and did serendipity play a part in this work?**

The analysis of the supramolecular structure of chloroazine **2** was difficult and nontrivial. It was a big surprise to find that crystals of **2** form a "kryptoracemate". Of course, azines are helical because of the  $\text{N}\cdots\text{N}$  bond conformation and crystals of azines usually contain "true racemates", equal numbers of enantiomers with opposite helicities (*M* and *P*). In kryptoracemates, however, the molecules of opposite helicity have different geometries, they are diastereomers **A**(*M*) and **B**\*(*P*). This serendipitous discovery is exciting and has already developed a life of its own. With the proper understanding of chloroazine **2**, we discovered several other kryptoracemates dormant in our crystal archive. Kryptoracemates are extremely rare and all known cases involve co-crystals of molecules with opposite chirality because of the presence of one or more chiral centers. Azines are fundamentally different in that their helicity is a function of the  $\text{N}\cdots\text{N}$  bond conformation and chirality results in the absence of chiral centers. It is a fascinating question why a kryptoracemate may become advantageous for kinetic or even thermodynamic reasons.

## COVER PROFILE

*"Azines are fundamentally different in that their helicity is a function of the N–N bond conformation and chirality results in the absence of chiral centers."* This and more about the story behind the front cover can be found in the article at 10.1002/chem.202400182).



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