# Controlling Dichroism of Molecular Crystals by Cocrystallization

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S *Supporting Information*

ABSTRACT: A combined crystallographic and optical properties study offers a simple model for the dichroic behavior of crystalline azobenzene chromophores, leading to a cocrystallization strategy to manipulate their solid-state arrangement and, therewith, dichroic behavior. This supramolecular strategy represents the first entry of crystal engineering into the design of dichroism in organic crystals.
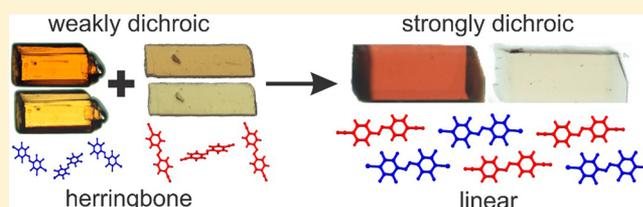
The understanding and control of light–matter interactions are central to modern materials chemistry,[1–6] directed toward developing new materials for manipulating light, such as waveguides,[7] switches,[8,9] light-harvesting[10–13] and nonlinear optics applications,[14] or for conducting photochemical reactions.[15,16] Cocrystallization, i.e., the formation of solid-state molecular complexes through designs based on well-defined supramolecular interactions,[17,18] has been particularly successful in making new organic solids with improved physicochemical properties.[19,20] In the context of light–matter interactions, particularly successful uses of cocrystallization have been in directing photochemical [2 + 2] photodimerization of olefins[21–23] and polymerization of di- and triacetylenes.[24,25] Besides these applications there has been surprisingly little exploration of how cocrystallization can be used to manipulate optical properties of organic solids,[26–32] considering that one of the first applications of cocrystallization was for generating organic crystals with advanced optical properties.[33,34]

Focusing on visible light, and using azobenzene (azo) model chromophores, we now demonstrate a cocrystallization-based approach to control dichroism, i.e., the difference in absorption of polarized light dependent on the orientation of its polarization,[35–37] in organic crystals. Although optical dichroism has been known for a long time in organic crystals,[38,39] and was recently utilized to design photoswitchable microporous materials and investigate molecular assembly on surfaces,[40,41] a strategy to control dichroic behavior of crystals by manipulating their structure has not yet been reported. The herein presented strategy permits crystal engineering[42–44] of optically dichroic crystals by using well-defined supramolecular interactions, such as halogen bonding, to direct the alignment of light-absorbing chromophores.[45–48]

As our first entry into investigation of dichroism in azo crystals, we noted that single crystals of two chemically similar azobenzenes, *trans*-bis(4-bromo-2,3,5,6-tetrafluorophenyl)-diazene (*trans*-**1**) and its iodo-analogue *trans*-bis(4-iodo-2,3,5,6-tetrafluorophenyl)diazene (*trans*-**2**) (Figure 1a),[49] exhibit very different optical properties if observed in plane-polarized light under a transmission optical microscope. Single crystals of *trans*-**1** exhibit strong dichroism (Figure 1b,c): in one

orientation of the polarizer the crystals appear dark orange but turn almost colorless upon 90° rotation.

Importantly, this observation was found *not to depend on the crystal face being observed*. In contrast, the perceived color of a *trans*-**2** single crystal changes much less upon polarizer rotation (Figure 1d,e). The difference in dichroism of *trans*-**1** and -**2** crystals cannot be explained by differences in chemical structure or conformation, as both molecules are rigid and structurally similar. Therefore, we turned to differences in crystal structures. In their respective single crystals, the compounds exhibit very different alignments of azo chromophores. In the highly dichroic *trans*-**1**, molecules are arranged with their longest molecular axes aligned in parallel, while in *trans*-**2** they adopt a herringbone orientation (Figure 1f,g). These differences offer an explanation for dichroic behavior. Namely, the absorption of light by the azo group depends on the orientation of its transition dipole moment, whose magnitude is related to molecular dimensions: the longest molecular axis roughly approximates the direction of the largest transition dipole moment (Figure 1h).[50,51] Plane-polarized light is expected to be most strongly absorbed by the azo chromophore if the direction of polarization coincides with the longest molecular axis.[52,53] It follows that a crystal structure in which the longest axes of all chromophores are aligned in parallel would make the absorption of plane-polarized light highly dependent on the orientation of the plane of light polarization with respect to the crystal.[40,41] It is important to distinguish that with such an arrangement dichroism should be observed *regardless of the crystal face being observed* (Supporting Information Figure S1). The behavior and crystal structure of *trans*-**1** are consistent with this expectation. Conversely, a crystal structure with a nonparallel orientation of neighboring molecular dipoles should almost always allow strong interaction between chromophores and plane-polarized light. Therefore, a herringbone-type structure is expected to be weakly dichroic or not at all, as indeed is observed for *trans*-**2**.
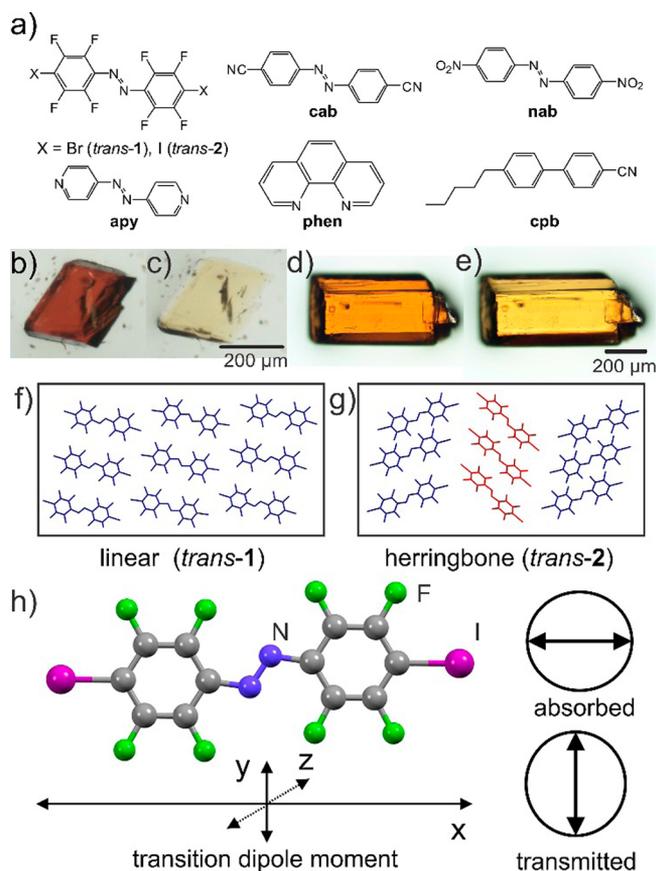
Figure 1. (a) Azobenzenes and cocrystal formers used in this study. Images of single crystals of (b and c) *trans*-**1** and (d and e) *trans*-**2**, each viewed in plane-polarized light with two perpendicular orientations of the polarizer. Molecular packing motifs in crystals of (f) *trans*-**1** and (g) *trans*-**2**, responsible for strong and weak dichroic behavior, respectively. (h) Schematic representation of the azo chromophore transition dipole moment, with arrow length representing its magnitude.

The aforementioned rationalization implies that inducing solid-state dichroism in crystalline organic solids is a question of circumventing herringbone arrangements, which is a problem already encountered in crystal engineering, e.g., in the design of organic semiconductors.[54−59] This suggests a means to manipulate dichroism of azo crystals by adjusting the spatial alignment of chromophores through cocrystal formation.[60−64] The azo chromophore is a suitable model for this purpose due to its rigid and linear shape. To verify the preceding hypothesis, we first turned to optical properties of the recently reported[65] cocrystals of *trans*-**1** and -**2** with *trans*-azopyridine (apy). The cocrystals (*trans*-**1**)(apy) and (*trans*-**2**)(apy) are reported to consist of linearly aligned halogen-bonded chains held together by Br···N and I···N interactions.[65−68] Therefore, both cocrystals should exhibit notable dichroism which is, indeed, observed (Figure S2, Supporting Information).

Next, we prepared two azo compounds anticipated to form structured cocrystals similar to those of apy: *trans*-4,4′-dinitroazobenzene (nab) and *trans*-4,4′-dicyanoazobenzene (cab) (Figure 1a). Crystal structure analysis of pure nab and cab reveals a herringbone arrangement of azo groups (Figure S3, Supporting Information), and, consequently, neither compound exhibits notable dichroism (Figure 2a and
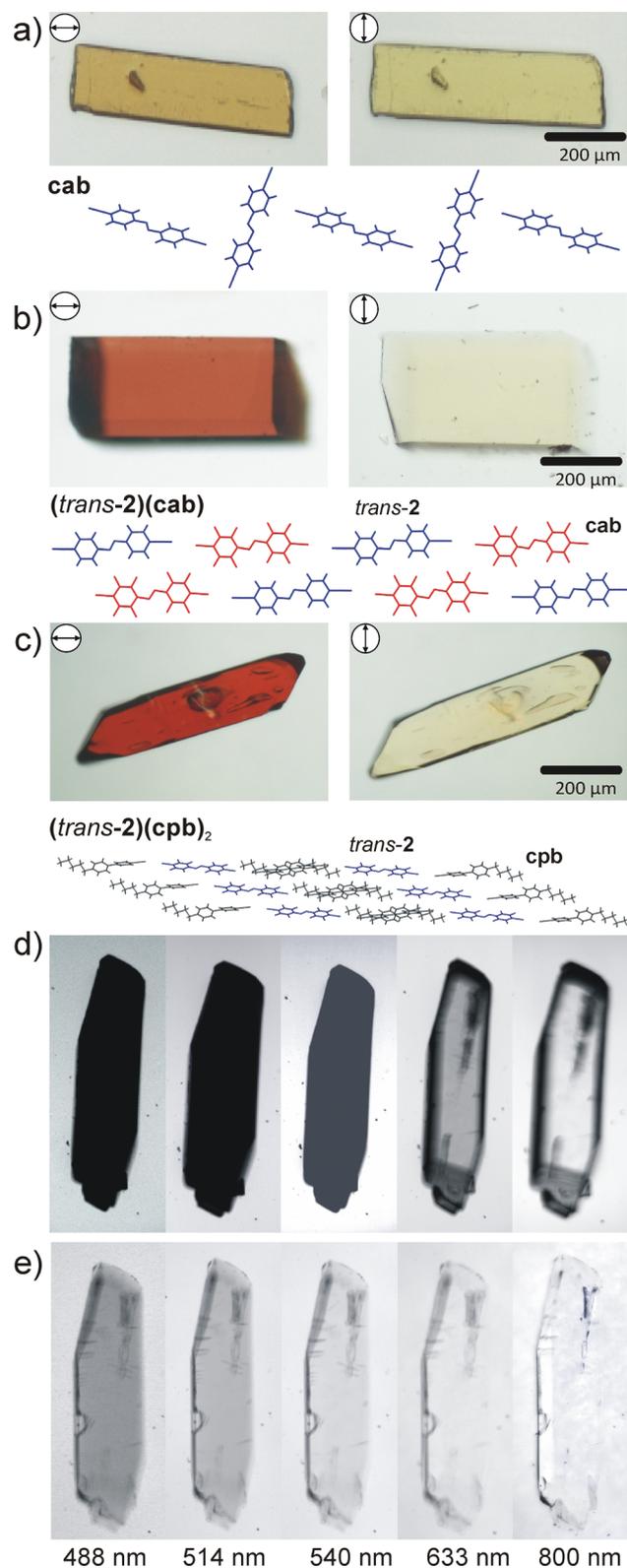

Figure 2. Single crystal, viewed in plane-polarized light with two mutually perpendicular orientations of the polarizer, and a general view of the solid-state packing of azo chromophores for (a) the (011) face of cab, (b) the (001) face of (*trans*-**2**)(cab), and (c) the (001) face of (*trans*-**2**)(cpb)$_2$. The actual orientation of azo chromophores for the (011) face of cab and the (001) face of (*trans*-**2**)(cab) is given in Supporting Information Figure S4. (d and e) Transmission images of a single crystal of (*trans*-**2**)(nab) taken using single-wavelength radiation, with two mutually perpendicular polarizer orientations.

Supporting Information Figure S2). Cocrystallization of cab with *trans*-**2** yields (*trans*-**2**)(cab), based on chains held by cyano⋯iodo halogen bonds (I⋯N distance, 2.973(2) Å; Figures S3 and S4, Supporting Information).[69] As in apy cocrystals, the halogen-bonded chains pack to form a structure that contains all azo groups aligned in parallel. Consistent with such a structure, the cocrystals are strongly dichroic, which is clearly seen for the (001) face of (*trans*-**2**)(cab), compared to the (011) face of cab (Figure 2b and Supporting Information Figure S4), which demonstrates the ability to generate a highly dichroic material from otherwise poorly dichroic components. A comparison of polarized light transmission for these two sets of faces with respect to crystal orientation is given in the Supporting Information Figure S5. Similar behavior is observed for (*trans*-**2**)(nab) cocrystals, composed of linear halogen-bonded chains, based on I⋯O halogen bonds involving nitro groups[69,70] as acceptors (I⋯O distances, 3.114(2) and 3.411(2) Å; Figure S3, Supporting Information). Again, the chains are arranged in parallel, enabling highly dichroic behavior (Figures S2 and S3, Supporting Information).

In order to enhance dichroism by using cocrystal formers that are not azobenzenes, we explored cocrystallization of *trans*-**2** with 4-cyano-4′-*n*-pentylbiphenyl (cpb). In addition to the nitrile group as a halogen bond acceptor, cpb also offers an aliphatic chain that should encourage the formation of layers in which the azo groups are aligned in parallel via halogen bonds and alkyl chain interdigitation.[71,72] Crystal structure analysis of (*trans*-**2**)(cpb)$_2$ reveals the expected layers containing parallel-aligned *trans*-**2** molecules, held together by cyano⋯iodo interactions (I⋯N distance, 3.08(2) Å) and alkyl group interdigitation. As a result, (*trans*-**2**)(cpb)$_2$ is strongly dichroic, demonstrating the rational formation of an organic dichroic material from one poorly dichroic and one optically transparent component (Figure 2c and Supporting Information Figure S4). We also tested the (*trans*-**2**)(nab) cocrystal as a single-wavelength dichroic filter. Consistent with the UV−vis absorption spectra of individual *trans*-**2** and nab, the cocrystal exhibits efficient dichroism up to 633 nm, after which nearly all light intensity is transmitted (Figure 2d,e). It is important to stress that the linear arrangement of chromophores results in the strongly dichroic crystals regardless of the face being examined. This behavior can be illustrated by a batch of (*trans*-**2**)(cpb)$_2$ or (*trans*-**2**)(cab) crystals exposing a variety of crystal faces. All of the crystals are strongly dichroic and change color from orange-red to colorless upon polarizer rotation (Figure 3).

An excellent verification of the proposed model of dichroism in azo crystals is given by the cocrystal of *trans*-**1** with 1,10-phenanthroline (phen). In contrast to *trans*-**1**, whose single crystals are highly dichroic regardless of the crystal face being observed, the dichroism of (*trans*-**1**)(phen) is highly dependent on the crystal face being inspected. Observation normal to the (0$\bar{1}$1) face reveals only very weak dichroism (Figure 4a), but if viewed normal to the (310) face, the cocrystal appears highly dichroic (Figure 4b). Variation in the intensity of transmitted light with respect to crystal orientation is roughly 10 times higher for the (310) face compared to the (0$\bar{1}$1) face. This is remarkable, as crystal thickness along the (310) direction is double that along the (0$\bar{1}$1) direction (Figure 4c).

The dichroic properties of (*trans*-**1**)(phen) are readily explained by its crystal structure which consists of π-stacked layers of phen and *trans*-**1** (Figure 4d) parallel to the crystallographic *ab*-plane. In each layer, phen molecules are connected by C−H⋯N hydrogen bonds (C⋯N distances,
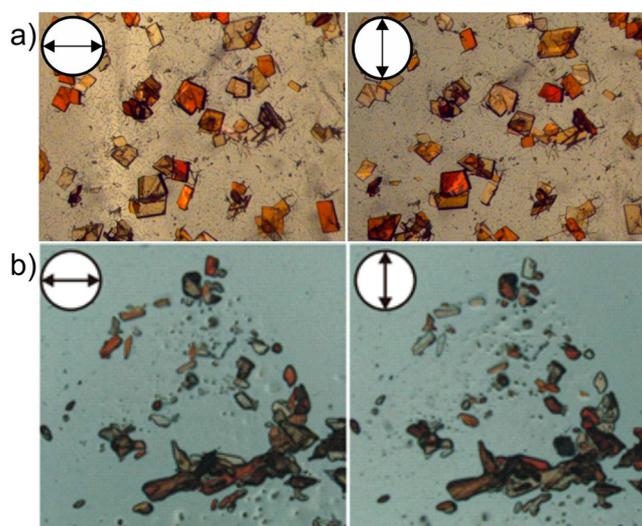

Figure 3. Views of a batch of crystals of (*trans*-**2**)(cab) (a) and (*trans*-**2**)(cpb)$_2$ (b) in plane-polarized light in mutually perpendicular orientations. The few crystals that seem to not change color are also dichroic but have a transition dipole moment axis not coinciding with either of the two selected polarizer orientations.
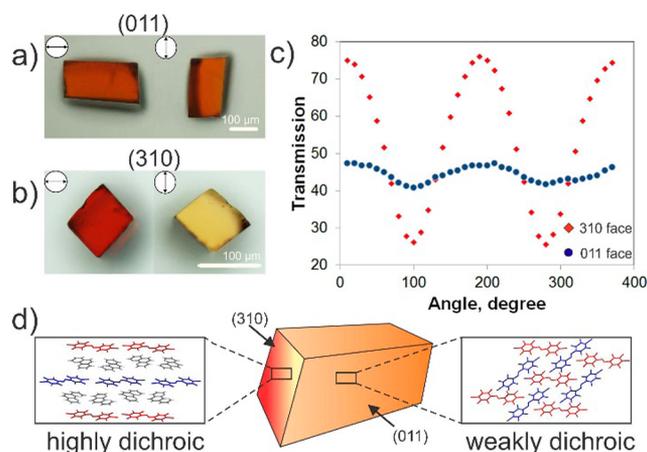

Figure 4. Views of a single crystal of (*trans*-**1**)(phen) in plane-polarized light, each with two perpendicular orientations of the polarizer: (a) perpendicular to the (0$\bar{1}$1) face and (b) perpendicular to the (310) face. (c) Difference in transmission of polarized light by a (*trans*-**1**)(phen) cocrystal at (310) and (0$\bar{1}$1) crystal faces. (d) Azobenzene chromophore orientations for the highly dichroic (310) face (left) and the weakly dichroic (0$\bar{1}$1) face (right). Phen molecules were omitted for clarity.

3.501(3) and 3.410(3) Å; Figure S3, Supporting Information), while *trans*-**1** molecules mutually associate via Br⋯Br interactions (Br⋯Br distance, 3.824(1) Å; Figure S3, Supporting Information). Whereas the azo chromophores are aligned in parallel in each *trans*-**1** layer, molecules in consecutive layers of *trans*-**1** are mutually rotated by 45°. Consecutive layers of *trans*-**1** therefore function as inherent crossed polarizers, which results in only slight dichroism along the (0$\bar{1}$1) direction (Figure 4d). Along the (310) direction, however, all azo groups in (*trans*-**1**)(phen) appear aligned, leading to strong dichroic behavior.

In summary, we have described a methodology to control optical dichroic properties of crystals of azobenzene chromophores by cocrystallization. Parallel assembly of azo building

blocks was identified as a prerequisite to obtain highly dichroic crystals, which was achieved by utilizing strongly directional interactions, such as halogen bonds. In this way, it was possible to generate highly dichroic materials from organic building blocks which, on their own, do not exhibit solid-state dichroism. Conversely, the herringbone packing is conducive of nondiscriminative light absorption, leading to nearly perfect isotropic optical properties at certain crystal faces. We believe that the presented work provides an important step forward in the understanding and design of optical properties of crystalline organic solids,[73−80] with specific applications as optical filters and polarizers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b01361.

> Details of synthesis and cocrystallization experiments, images of selected cocrystals in polarized light, detailed images of crystal structures of herein reported cocrystals, selected Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra, and thermal analysis data (PDF)

Accession Codes

CCDC 1400996−1401001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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