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Determining Molecular Orientations in Disordered Materials from X-ray Linear Dichroism at the Iodine L₁-Edge

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Supporting Information Placeholder

ABSTRACT: We demonstrate that measurements of X-ray linear dichroism are an effective method for determining bond orientations in disordered materials, by reporting the first observation of X-ray linear dichroism at the iodine L₁-edge. The iodine-containing molecular solid studied in this work was the inclusion compound containing 4,4'-diiodobiphenyl guest molecules in the perhydrotriphenylene host structure. In this material, the guest substructure does not exhibit three-dimensional ordering, and therefore diffraction-based techniques do not provide insights on the orientational properties of the guest molecules. Iodine L₁-edge X-ray absorption spectra, recorded as a function of orientation of a single crystal of the material, exhibit significant dichroism (whereas no dichroism is observed at the iodine L₂-edge and L₃-edge). From quantitative analysis of the X-ray dichroism, the orientational properties of the C–I bonds within this material are established. The results pave the way for applying X-ray dichroism to determine molecular orientational properties of other materials, especially for partially ordered materials such as liquid crystals, confined liquids and disordered crystalline phases for which diffraction techniques may not be applicable.

While the interaction of linearly polarized visible light with anisotropic materials is well understood and widely exploited (e.g. in the polaroid sheet¹ and the polarizing optical microscope²), substantially less attention has been devoted to studies of the interaction of linearly polarized X-rays with materials. However, recent studies of X-ray linear dichroism³ and X-ray birefringence⁴ have elucidated a deeper understanding of these phenomena, which refer to the fact that the X-ray absorption coefficient (in the case of dichroism) and the refractive index (in the case of birefringence) of an anisotropic material depend on the orientation of the material relative to the direction of polarization of a linearly polarized incident X-ray beam. In the absence of diffraction, X-ray dichroism and X-ray birefringence are observed close to an absorption edge of a selected element within the material, and arise due to local anisotropy in the bonding environment of the selected type of atom. Thus, unlike their optical analogues,⁵ X-ray dichroism and X-ray birefringence are sensitive to the local orientational properties of individual molecules and chemical bonds, rather than the overall symmetry properties of the material.

The phenomena of X-ray dichroism and X-ray birefringence have the potential to be harnessed in a range of analytical techniques and devices. For example, solid inclusion compounds containing brominated organic molecules have been shown to func-

tion as effective X-ray dichroic filters.^{3b-d} In this case, X-ray photons with polarization parallel to the C–Br bond axis in the material are preferentially attenuated over those with polarization perpendicular to this axis. Such dichroic filter materials have a range of potential applications, such as in polarization analysis of magnetic X-ray scattering^{3b} and for X-ray polarimetry devices in astronomy.^{3d} Measurements of X-ray birefringence have also been used to determine the orientational properties of specific bonds in solids.^{4c,d} In particular, the X-ray Birefringence Imaging (XBI) technique,^{4h-j} which represents the X-ray analogue of the polarizing optical microscope, enables measurements of X-ray birefringence to be carried out in a spatially resolved manner and yields information on the size, spatial distribution and temperature dependence of orientationally distinct domains in materials.

Most previous research on X-ray dichroism and X-ray birefringence has focused on brominated organic materials using incident polarized X-rays at the bromine K-edge. However, in order to exploit the full potential of these phenomena and to apply them to a wider range of problems in materials science, experiments at different absorption edges are required. In particular, on moving to elements of higher atomic number, the energy of the K-edge may be too high to be readily accessible at synchrotron facilities, and it is then relevant to explore the capability of using the lower-energy L-edges instead.

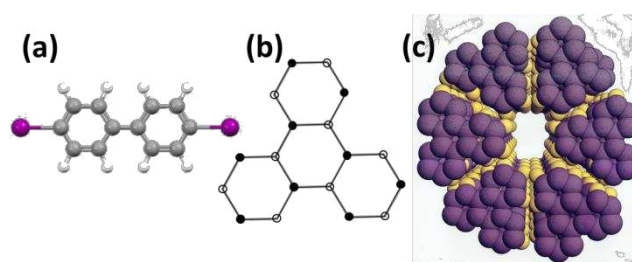


Figure 1. Molecular structures of (a) 4,4'-diiodobiphenyl (DIBP) and (b) perhydrotriphenylene (PHTP). (c) The tunnel host structure in PHTP inclusion compounds (guest molecules not shown).

In pursuit of this goal, we report here the first studies of X-ray dichroism at the iodine L₁-edge; specifically, by studying the dependence of the X-ray absorption spectrum on the orientation of a single crystal of a material containing iodinated organic molecules, the orientational characteristics of the C–I bonds have been established. The material studied is a solid inclusion compound⁶ containing 4,4'-diiodobiphenyl (DIBP; Fig. 1a) guest molecules within the perhydrotriphenylene (PHTP; Fig. 1b) host tunnel

structure. Inclusion compounds of PHTP are constructed from stacks of PHTP molecules, forming one-dimensional tunnels (Fig. 1c) with elliptical cross-section (the van der Waals diameter of the tunnel is in the range *ca.* 4 – 7 Å and the inter-tunnel separation is *ca.* 14 – 15 Å). The PHTP host tunnel can accommodate a wide range of different types of guest molecule.⁷ The specific physico-chemical properties that result from the inclusion phenomenon may be exploited in a range of applications, such as “molecular reaction vessels” for stereo-selective polymerization reactions,⁸ or as non-linear optical⁹ and pyroelectric¹⁰ materials. PHTP inclusion compounds containing linear conjugated dyes as guest molecules can also perform efficient photon down-conversion and have potential uses in optoelectronic applications, including light-emitting diodes, photovoltaics and silicon detectors.¹¹ We emphasize that several of these applications of PHTP inclusion compounds (or other types of solid inclusion compound) rely on exploiting the inclusion phenomenon as a strategy to *control* the orientational characteristics of the guest molecules, and it is therefore crucial that techniques are available to allow molecular orientational distributions in such materials to be established independently of X-ray diffraction data, particularly when there is *positional* disorder of the guest molecules in the host structure.

Single-crystal X-ray diffraction rotation photographs¹² of the DIBP/PHTP inclusion compound (recorded at ambient temperature) indicate that the X-ray scattering from the guest component comprises two-dimensional diffuse sheets in reciprocal space, from which it is concluded that the guest molecules are ordered only along each individual tunnel. Furthermore, there is an incommensurate relationship¹³ between the periodicities of the host (c_h) and guest (c_g) substructures along the tunnel direction [$c_g = 14.9(2)$ Å, $c_h = 4.74(2)$ Å, $c_g/c_h \approx 3.14$]. In addition to the lack of three-dimensional positional ordering described above, the guest molecules in PHTP inclusion compounds can exhibit various other types of disorder,¹⁴ such as dynamic disorder by reorientation about the axis of the host tunnel. However, in spite of these aspects of disorder, the guest molecules may still have well-defined orientational properties relative to the PHTP host structure, as a consequence of the structural constraints imposed on the guest molecules by confinement within the host tunnel structure. Given that the guest substructure is only ordered in one-dimension, and therefore does not give sharp Bragg maxima in the single-crystal X-ray diffraction pattern, alternative approaches are required to gain insights into the orientational characteristics of the guest molecules in these materials. In this paper, we explore the opportunity to determine the orientational properties of the guest molecules in the DIBP/PHTP inclusion compound from iodine L_1 -edge X-ray dichroism data.

X-ray absorption spectra were recorded in transmission at ambient temperature for a single crystal of the DIBP/PHTP inclusion compound on beamline I16 at Diamond Light Source,¹⁵ using the set-up in Fig. 2 (full experimental details are given in SI). The single crystal studied had a long-needle morphology (with distorted hexagonal cross-section) and overall dimensions $0.50 \times 0.75 \times 4.0$ mm³. Fig. 3 shows the X-ray absorption spectra recorded in the vicinity of the iodine L_1 , L_2 and L_3 edges (spanning the energy range *ca.* 4.5 – 5.2 keV), with the tunnel axis of the PHTP host structure (parallel to the long axis of the needle-shaped crystal morphology) oriented parallel ($\chi = 0^\circ$; red data in Fig. 3) or perpendicular ($\chi = 90^\circ$; green in Fig. 3) to the direction of linear polarization of the incident X-ray beam.

At the iodine L_1 -edge (Fig. 3a), the absorption of the linearly polarized X-rays depends strongly on crystal orientation, with highest absorption when the tunnel axis of the PHTP host structure is parallel to the direction of polarization of the incident X-ray beam (i.e. $\chi = 0^\circ$), and significantly lower absorption when the tunnel axis is perpendicular to the direction of polarization of

the incident X-ray beam (i.e. $\chi = 90^\circ$). The difference between the X-ray absorption spectra recorded for $\chi = 0^\circ$ and $\chi = 90^\circ$ gives the X-ray dichroism data. The maximum X-ray dichroism arises at an incident X-ray energy of $E = 5.188$ keV.

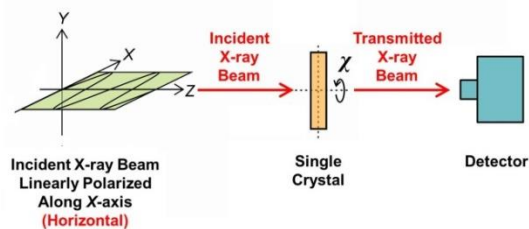


Figure 2. Experimental set-up for X-ray dichroism studies. The incident X-ray beam propagates along the z -axis and is almost entirely linearly polarized along the x -axis. The crystal orientation angle χ is defined, with $\chi = 90^\circ$ in the crystal orientation shown.

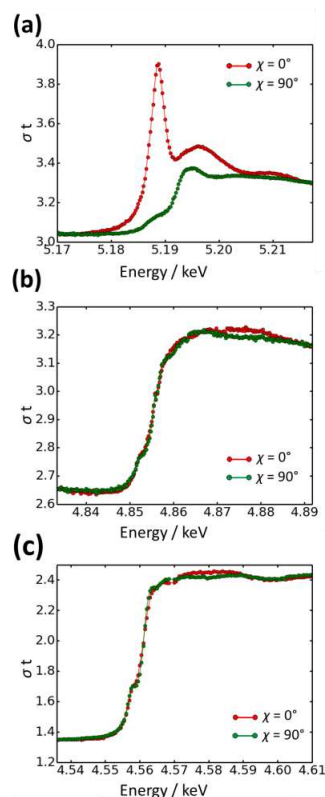


Figure 3. X-ray absorption spectra recorded for a single crystal of the DIBP/PHTP inclusion compound as a function of energy close to: (a) the iodine L_1 -edge, (b) the iodine L_2 -edge and (c) the iodine L_3 -edge, with the tunnel axis of the PHTP host structure parallel ($\chi = 0^\circ$; red data) or perpendicular ($\chi = 90^\circ$; green data) to the direction of linear polarization of the incident X-ray beam.

As X-ray linear dichroism in the vicinity of the L_1 -edge is dictated by the orientational characteristics of the C–I bonds in the material, our results suggests that the DIBP guest molecules are oriented with the C–I bonds close to parallel to the tunnel axis of the PHTP host structure. The strong dichroic resonance observed at $E = 5.188$ keV arises from promotion of an iodine $2s$ core electron to the σ^* anti-bonding orbital associated with the C–I bond, which has mixed s-p character at the iodine site. The anisotropy of the X-ray absorption reflects the strong anisotropy of the $\sigma^*(C-I)$ anti-bonding orbital. The probability of the $2s(I) \rightarrow \sigma^*(C-I)$ transition depends strongly on the orientation of the vacant $\sigma^*(C-I)$ anti-bonding orbital relative to the direction of linear polarization of the incident X-ray beam, and the highest transition probability

arises when the C–I bond is parallel to the direction of polarization of the incident X-ray photons (i.e. for $\chi = 0^\circ$).

While our data at the iodine L₁-edge are consistent with the C–I bonds lying close to parallel to the tunnel axis of the PHTP host structure, a small peak is observed at $E = 5.188$ keV in the data recorded at $\chi = 90^\circ$ (Fig. 3a) which suggests that the C–I bond vector has a non-zero component in the plane perpendicular to the tunnel axis, such that the symmetry requirements for the $2s(\text{I}) \rightarrow \sigma^*(\text{C–I})$ transition are satisfied at $\chi = 90^\circ$, albeit with low probability. We suggest that this small peak arises from a slight tilting of the C–I bonds of the DIBP guest molecules away from the tunnel axis of the PHTP host structure.¹⁶ As now described, quantitative analysis of the X-ray dichroism observed at the iodine L₁-edge allows the tilt angle ψ (defined in Fig. 4) of the C–I bond with respect to the PHTP tunnel axis to be estimated.

We now consider geometric aspects (i.e. the orientation and polarization dependence) of X-ray linear dichroism at the iodine L₁-edge for iodinated organic materials containing C–I bonds. By applying the compact and powerful formalism of spherical tensors, we can build on results derived in the literature^{3a,17} which provide a complete description of geometric properties of the X-ray absorption process, given a known set of tensor components. Our first task is to calculate the tensor components for the dipole absorption cross-section, based on the assignment that the sharp spectral line at $E = 5.188$ keV in the iodine L₁-edge spectrum arises from the $2s(\text{I}) \rightarrow \sigma^*(\text{C–I})$ transition, which occurs from an s -state to an empty anti-bonding orbital for which the p -projection lies along the C–I bond. Taking the quantization axis (z -axis) as the direction of the C–I bond, the initial-state $|i\rangle$ and final-state $|f\rangle$ wavefunctions are:

$$|i\rangle \propto Y_0^0 = +1$$

$$|f\rangle \propto Y_0^1 = [f_{-1}^1, f_0^1, f_{+1}^1] = [0, 1, 0]$$

All transitions therefore correspond to zero change in the angular momentum projection, so (from Eqn 6.4 in ref. 3a) we can select $\mu = \mu' = 0$, which leads to very simple expressions for the tensor components of the dipole absorption cross-section in terms of a single Clebsch-Gordon coefficient:

$$\sigma_Q^K = A(1, 0, 1, 0 | K, Q)$$

where A is a constant factor that contains terms such as radial integrals. The non-zero values of σ_Q^K are:

$$\sigma_0^0 = +A \quad \text{and} \quad \sigma_0^2 = -\sqrt{2}A$$

where σ_0^0 is a scalar and σ_0^2 is a quadrupole directed along the C–I bond.

For the case in which the C–I bond lies in the plane perpendicular to the direction of propagation of the incident beam, and using θ to denote the angle between the photon polarization vector and the C–I bond, it can be shown (see Eqn 4.4 in ref. 3a) that, assuming uniaxial anisotropy, the X-ray absorption coefficient has the following dependence on θ :

$$\sigma(\theta) \propto \cos^2 \theta$$

In our experimental set-up (Fig. 2), the crystal orientation is specified by the angle χ between the tunnel axis of the PHTP host structure and the direction of polarization of the incident X-ray beam, whereas the equations above refer to the angle θ between the C–I bond and the direction of incident polarization. The fact that the peak at $E = 5.188$ keV is significantly more intense (Fig. 3a) for $\chi = 0^\circ$ than for $\chi = 90^\circ$ indicates that the orientation of the C–I bond must be close to the direction of the tunnel axis of the PHTP host structure. Nevertheless, the non-zero intensity observed for this peak at $\chi = 90^\circ$ suggests that the C–I bond direc-

tion is tilted from the host tunnel axis. We incorporate this situation into a revised model¹⁸ in which the C–I bond is tilted from the tunnel axis by an angle ψ and with disorder (dynamic or static) of the C–I bond by reorientation about the tunnel axis. In this model, the resultant disordered system is still uniaxial. The averaging due to disorder has no effect on the scalar part and does not introduce any new tensor components, and the only effect is to re-scale the quadrupole term as follows:

$$\sigma_0^2(\psi, \chi) = -\sqrt{2} \times (3\cos^2 \psi - 1)/2$$

leading to a modified equation for X-ray absorption coefficient:

$$\sigma(\psi, \chi) \propto 1 + (3\cos^2 \psi - 1)(3\cos^2 \chi - 1)/2$$

From this equation, the maximum X-ray absorption (at $\chi = 0^\circ$) is decreased and the minimum X-ray absorption (at $\chi = 90^\circ$) is increased, relative to a situation in which the C–I bond is parallel to the tunnel axis (i.e. $\psi = 0^\circ$). Consequently, the ratio (denoted R) of the X-ray absorption coefficients for the $\chi = 90^\circ$ (denoted σ_\perp) and $\chi = 0^\circ$ (denoted σ_\parallel) orientations is non-zero, and is given by:

$$R = \sigma_\perp / \sigma_\parallel = 1/2 \tan^2 \psi$$

From fitting the X-ray absorption spectra in Fig. 3a (details of the fitting procedure are given in SI) to establish the ratio of the intensity of the peak at $\chi = 90^\circ$ to the intensity of the peak at $\chi = 0^\circ$, we obtain¹⁹ $R = 0.0514$, from which the (average) value of the tilt angle ψ is determined to be $\psi = 17.8^\circ$. From the fitting procedure (see SI), the error in the value of R is ± 0.006 , leading to an estimated error in ψ of *ca.* $\pm 1.0^\circ$.

This result demonstrates that analysis of X-ray linear dichroism data at the iodine L₁-edge may be exploited to determine the orientational properties of C–I bonds in disordered materials. In the case of the DIBP/PHTP inclusion compound (and other composite guest/host materials), such information cannot be obtained from X-ray diffraction data due to the disordered nature of the guest molecules, encompassing both the lack of 3-dimensional positional ordering as well as disorder with respect to guest molecules sampling different orientations (either on a static or dynamic basis) with respect to reorientation around the tunnel axis. Our conclusion that the axis of the DIBP guest molecule is tilted relative to the tunnel axis of the PHTP host structure is consistent with the fact that the reported¹² (from analysis of X-ray diffraction rotation photographs) periodic repeat distance of the guest molecules along the tunnel [$c_g = 14.9(2)$ Å] is *shorter* than the van der Waals length of the guest molecule (estimated to be 15.2 Å).

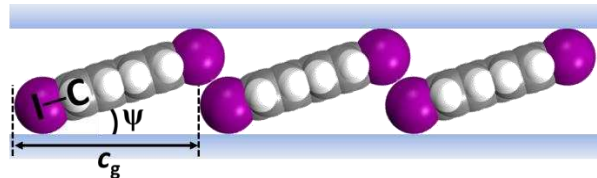


Figure 4. Schematic of the arrangement of DIBP guest molecules in the PHTP tunnel determined from quantitative analysis of the iodine L₁-edge X-ray dichroism data. The tilt angle (ψ) and periodic repeat distance (c_g) of the guest molecules are indicated.

In contrast to the behaviour at the iodine L₁-edge, no significant dichroism is observed at the L₂-edge or the L₃-edge (Fig. 3b,c and SI). Thus, at the L₂-edge and L₃-edge, the X-ray absorption spectrum is essentially identical for the $\chi = 0^\circ$ and $\chi = 90^\circ$ orientations. The transitions at the L₂-edge and L₃-edge involve promotion of a $2p(\text{I})$ electron to an empty s -state or d -states, which occur in an essentially isotropic manner. We note that the absorption corresponding to the L₃-edge is twice the magnitude of that for the L₂-edge, as the L₃-edge originates from the degenerate $2p_x$ and $2p_y$ orbitals whereas the L₂-edge originates from the $2p_z$ orbital. It is

noteworthy that the XANES regions of the iodine L₂-edge and L₃-edge X-ray absorption spectra are relatively "featureless" (compared to the L₁-edge X-ray absorption spectrum), consistent with previous observations for iodo-organic materials,²⁰ and for molecular iodine and polyiodide anions in different environments.²¹

We have reported the first X-ray dichroism study at the iodine L₂-edges and have shown that measurements at the L₁-edge are an effective analytical method for determining C–I bond orientations in iodinated organic materials. This strategy is particularly useful when X-ray diffraction techniques are not applicable, for example in the case of materials that lack three-dimensional translational periodicity. Accessing the L₁-edge (rather than the higher-energy K-edge) allows such techniques to be applied to study elements of higher atomic number, and extends the opportunity to apply techniques based on polarized X-rays to a much wider range of materials. Thus, the results reported here pave the way for applying X-ray dichroism measurements to study the orientational properties of important iodine-containing materials, such as iodinated liquid crystals, halogen-bonded materials, polarizing films, X-ray contrast agents and materials comprising self-assembled monolayers.^{22,23} Another promising strategy to widen the scope of iodine L₁-edge X-ray dichroism is to dope non-iodine containing materials with iodine (e.g. by iodo-substitution of organic molecules in place of F, Cl, Br or H) to produce a dichroic probe that may be exploited to "report" on molecular orientation (in much the same way that tryptophans are engineered into proteins to study fluorescence anisotropy). Finally, we note that the strong X-ray dichroism exhibited by the DIBP/PHTP inclusion compound near the iodine L₁-edge suggests that this material could be used as an effective dichroic filter in X-ray polarization analysis.

ASSOCIATED CONTENT

Supporting Information

Details of materials preparation, experimental methods and the fitting procedure used for quantitative analysis of the X-ray dichroism data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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REFERENCES

- (1) Land, E. H. *J. Opt. Soc. Am.* **1951**, *41*, 957-963.
- (2) (a) *Practical Optical Crystallography*; Hartshorne, N. H.; Stuart, A.; Edward Arnold Publisher, London, 1969. (b) Kaminsky, W.; Claborn, K.; Kahr, B. *Chem. Soc. Rev.* **2004**, *33*, 514-525.
- (3) (a) Brouder, C. *J. Phys.: Condens. Matter* **1990**, *2*, 701-738. (b) Collins, S. P.; Laundry, D.; Harris, K. D. M.; Kariuki, B. M.; Bauer, C. L.; Brown, S. D.; Thompson, P. *J. Phys.: Condens. Matter* **2002**, *14*, 123-134. (c) Chao, M.-H.; Kariuki, B. M.; Harris, K. D. M.; Collins, S. P.; Laundry, D. *Angew. Chem. Int. Ed.* **2003**, *42*, 2982-2985.
- (4) (a) Templeton, D. H.; Templeton, L. K. *Acta Crystallogr. Sect. A* **1986**, *42*, 478-481. (b) Palmer, B. A.; Morte-Ródenas, A.; Kariuki, B. M.; Harris, K. D. M.; Collins, S. P. *J. Phys. Chem. Lett.* **2011**, *2*, 2346-2351. (c) Palmer, B. A.; Edwards-Gau, G. R.; Morte-Ródenas, A.; Kariuki, B. M.;

- Lim, G. K.; Harris, K. D. M.; Dolbnya, I. P.; Collins, S. P. *J. Phys. Chem. Lett.* **2012**, *3*, 3216-3222. (d) Joly, Y.; Collins, S. P.; Grenier, S.; Tolentino, H. C. N.; De Santis, M. *Phys. Rev. B* **2012**, *86*, 220101(R). (e) Collins, B. A.; Cochran, J. E.; Yan, Y. H.; Gann, E.; Hub, C.; Fink, R.; Wang, C.; Schuettfort, T.; McNeill, C. R.; Chabynyc, M. L. *et al. Nat. Mater.* **2012**, *11*, 536-543. (f) Palmer, B. A.; Edwards-Gau, G. R.; Kariuki, B. M.; Harris, K. D. M.; Dolbnya, I. P.; Collins, S. P. *Science* **2014**, *344*, 1013-1016. (g) Palmer, B. A.; Edwards-Gau, G. R.; Kariuki, B. M.; Harris, K. D. M.; Dolbnya, I. P.; Collins, S. P.; Sutter, J. P. *J. Phys. Chem. Lett.* **2015**, *6*, 561-567.
- (5) Optical birefringence depends on the anisotropy of the material as a whole. For a crystalline material, it depends on the overall symmetry of the structure. For an ensemble of molecules or fibres, it may depend on the net orientational properties of the ensemble.
- (6) (a) *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker, New York, Vol. 2, **2004**. (b) Harris, K. D. M. *Supramol. Chem.* **2007**, *19*, 47-53. (c) Palmer, B. A.; Harris, K. D. M.; Guillaume, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 5096-5100. (d) Palmer, B. A.; Le Comte, A.; Harris, K. D. M.; Guillaume, F. *J. Am. Chem. Soc.* **2013**, *135*, 14512-14515.
- (7) (a) Farina, M.; Di Silvestro, G.; Sozzani, P.; *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon Press, Oxford, Vol. 6, **1996**, pp. 371-398. (b) Couderc, G.; Hulliger, J. *Chem. Soc. Rev.* **2010**, *39*, 1545-1554. (c) König, O.; Bürgi, H. B.; Armbruster, T.; Hulliger, J.; Weber, T. *J. Am. Chem. Soc.* **1997**, *119*, 10632-10640.
- (8) Farina, M.; Audiso, G.; Natta, G. *J. Am. Chem. Soc.* **1967**, *89*, 5071.
- (9) (a) Hoss, R.; König, O.; Kramer-Hoss, V.; Berger, U.; Rogin, P.; Hulliger, J. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1664-1666. (b) Hulliger, J.; König, O.; Hoss, R. *Adv. Mater.* **1995**, *7*, 719-721.
- (10) (a) Hulliger, J. *Chem. Eur. J.* **2002**, *8*, 4578-4586. (b) Süß, H. I.; Wuest, T.; Sieber, A.; Althaus, R.; Budde, F.; Lüthi, H.-P.; McManus, G. D.; Rawson, J.; Hulliger, J. *CrystEngComm* **2002**, *4*, 432-439.
- (11) (a) Botta, C.; Patrinoiu, G.; Picouet, P.; Yunus, S.; Communal, J.-E.; Cordella, F.; Quochi, F.; Mura, A.; Bongiovanni, G.; Pasini, M. *et al. Adv. Mater.* **2004**, *16*, 1716-1721. (b) Alohyna, M.; Milián Medina, B.; Poulsen, L.; Moreau, J.; Beljonne, D.; Cornil, J.; Di Silvestro, G.; Cerminara, M.; Meinardi, F.; Tubino, R. *et al. Adv. Funct. Mater.* **2008**, *18*, 915-921.
- (12) König, O. PhD Thesis, University of Bern, Switzerland, **1996**, p. 69.
- (13) (a) Bak, P. *Rep. Prog. Phys.* **1982**, *45*, 587-629. (b) Rennie, A. J. O.; Harris, K. D. M. *Proc. Royal Soc. A* **1990**, *430*, 615-640. (c) Sun, J.; Lee, S.; Lin, J. *Chem. Asian J.* **2007**, *2*, 1204-1229.
- (14) (a) Mayo, S. C.; Proffen, T.; Bown, H.; Welberry, T. R. *J. Appl. Crystallogr.* **1999**, *32*, 464-471. (b) Weber, T.; Estermann, M. A.; Bürgi, H.-B. *Acta Crystallogr. Sect. B* **2001**, *57*, 579-590. (c) Sozzani, P.; Bovey, P. A.; Schilling, F. C. *Macromol.* **1989**, *22*, 4225-4230. (d) Schilling, F. C.; Sozzani, P.; Bovey, P. A. *Macromol.* **1991**, *24*, 4369-4375.
- (15) Collins, S. P.; Bombardi, A.; Marshall, A. R.; Williams, J. H.; Barlow, G.; Day, A. G.; Pearson, M. R.; Woolliscroft, R. J.; Walton, R. D.; Beutier, G. *et al. AIP Conf. Proc.* **2010**, *1234*, 303-306.
- (16) In principle, this observation could be caused by slight misalignment of the single crystal such that, in the $\chi = 90^\circ$ orientation, the tunnel axis is not perfectly perpendicular to the incident linear polarization. However, in our experiments (see SI for more details), accurate alignment was ensured by measuring diffraction data from the PHTP host structure using the diffractometer capability of beamline I16, then aligning the crystal with the tunnel axis strictly vertical for the measurement at $\chi = 90^\circ$. Measurements of X-ray absorption spectra were also repeated for several different crystals; in all cases, the weak peak at $E = 5.188$ keV was observed at $\chi = 90^\circ$, indicating that this peak is intrinsic in origin.
- (17) Lovesey, S. W.; Balcar, E.; Knight, K. S.; Fernández Rodríguez, J. *Phys. Rep.* **2005**, *411*, 233-289.
- (18) A similar model was developed previously^{4g} in the context of an X-ray birefringence imaging study of a different solid inclusion compound.
- (19) The ratio of the intensity of the peak at $\chi = 90^\circ$ to the intensity of the peak at $\chi = 0^\circ$ is equal to the ratio of absorption coefficients $\sigma_{\parallel}/\sigma_{\perp} = R$.
- (20) Schlegel, M. L.; Reiller, P.; Mercier-Bion, F.; Barré, N.; Moulin, V. *Geochim. Cosmochim. Acta* **2006**, *70*, 5536-5551.
- (21) Konishi, T.; Tanaka, W.; Kawai, T.; Fujikawa, T. *J. Synchrotron Rad.* **2001**, *8*, 737-739.
- (22) Ying, Y.; Dubey, M.; Bernasek, S. L.; Dismukes, G. C. *Langmuir* **2007**, *23*, 8257-8263.
- (23) Xiang, L.; Hines, T.; Palma, J. L.; Lu, X.; Mujica, V.; Ratner, M. A.; Zhou, G.; Tao, N. *J. Am. Chem. Soc.* **2016**, *138*, 679-687.

TOC Graphic

