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## PAPER



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# Assembly and dichroism of a fourcomponent halogen-bonded metalorganic cocrystal salt solvate involving dicyanoaurate(I) acceptors<sup>+</sup>

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We describe the use of dicyanoaurate ions as linear ditopic metal-organic acceptors for the halogen bond-driven assembly of a dichroic metal-organic cocrystal based on azobenzene chromophores. Structural analysis by single crystal X-ray diffraction revealed that the material is a four-component solid, consisting of anticipated anionic metal-organic halogen-bonded chains based on dicyanoaurate ions, as well as complex potassium-based cations and discrete molecules of the crown ether 15crown-5. Importantly, the structural analysis revealed the parallel alignment of the halogen-bonded chains required for dichroic behaviour, confirming that crystal engineering principles developed for the design of halogen-bonded dichroic organic cocrystals are also applicable to metal-based structures. In the broader context of crystal engineering, the structure of the herein reported dichroic material is additionally interesting as the presence of an ion pair, a neutral azobenzene and a molecule of a room-temperature liquid make it an example of a solid that simultaneously conforms to definitions of a salt, a cocrystal, and a solvate.

### Introduction

Halogen bonding has emerged as a powerful concept in crystal engineering<sup>1</sup> of molecular materials, enabling the deliberate synthesis of multi-component crystals (cocrystals),<sup>2,3</sup> as well as open framework structures or unusually complex solid-state architectures.<sup>4–6</sup> While the use of halogen bonding in

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controlling and directing the assembly of solid-state supramolecular architectures has been demonstrated, the applications of resulting solid-state cocrystal materials, *e.g.* in pharmaceutical materials science or as energetic materials,<sup>7,8</sup> are only now emerging, with the area of optically active materials being among those that are particularly well developed. Some of the notable examples of such materials include photo-reactive halogen-bonded cocrystals, in which the supramolecular assembly makes the solid material conducive to [2 + 2] photodimerisation or polymerisation,<sup>9</sup> emissive cocrystals in which halogen bonding enables modification of fluorescence emission,<sup>10</sup> as well as photo-mechanical<sup>11</sup> halogen-bonded cocrystals<sup>12,13</sup> which involve azobenzene (azo) chromophores and are capable of direct conversion of light into macroscopic mechanical motion of the crystal.

### Solid-state properties of azobenzene cocrystals

The above-noted development of photo-mechanical azobenzene cocrystals has been greatly facilitated by the discovery that extensive, but not necessarily complete, fluorination of the azobenzene moiety leads to considerable changes in its chemical reactivity,<sup>14</sup> including stabilisation of the normally highly elusive *cis*azobenzene molecular isomer.<sup>15,16</sup> Such stabilisation has enabled the otherwise tantalising isolation of simple *cis*-azobenzene derivatives in the form of single crystals.<sup>16</sup> This has not only allowed for their structural characterisation but also revealed the ability to undergo a light-induced *cis*  $\rightarrow$  *trans* transformation resulting in macroscopic motion and change in crystal shape.<sup>16,17</sup> Notable examples of such fluorinated azobenzenes are 4,4′-diiodooctafluoroazobenzene



**Fig. 1** (a) Schematic representation of *trans*-4,4'-diiodooctafluoroazobenzene, an azobenzene chromophore that can act as a halogen bond donor; (b) illustration of the magnitudes of the transition dipole moment in space for a molecule of *trans*-4,4'-diiodooctafluoroazobenzene. Illustrations of crystal engineering techniques for designing dichroic cocrystals based on halogen bonding with *trans*-4,4'-diiodooctafluoroazobenzene: (c) by using a linear ditopic halogen bond acceptor and (d) by using a halogen bond acceptor substituted with an aliphatic chain encouraging interdigitation and formation of a lamellar structure. Figures (b), (c) and (d) have been adapted from ref. 22 with permission.

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(Fig. 1a), as well as its 4,4'-dibromo derivative. The presence of an iodine or a bromine halogen atom on a highly electron-deficient fluorinated azobenzene moiety makes these molecules excellent halogen bond donors, enabling the synthesis not only of single-component photo-mechanical crystals, but also of two-component halogen-bonded cocrystals in which the photo-mechanical behavior of the azobenzene-based component can be fine-tuned through the presence of the halogen-bonding acceptor.<sup>12,13</sup>

### Controlling dichroism through halogen bond-driven cocrystallisation

Besides providing access to new photo-switchable molecular solids, this class of perfluorinated azobenzenes also enables the introduction and investigation of other optical properties in the solid state. A notable example is dichroism, 18-20 i.e. the ability of solid-state materials to absorb or transmit polarised light differently, depending on the orientation of polarisation. Whereas dichroism in molecular crystals has been known for a very long time,<sup>21</sup> it was only recently that the first simple model and a rational crystal engineering strategy to design dichroic crystals was reported.22 In particular, by using differently substituted azobenzene molecules as model chromophores we have demonstrated that the appearance of dichroism in a crystal requires their parallel alignment. This was rationalised by considering that the absorption of light by a molecule of an azobenzene depends on the orientation of its transition dipole moment. The magnitude of the transition dipole moment of a molecule is related to its molecular dimensions: the longest molecular axis of an azobenzene chromophore roughly approximates the direction of the largest transition dipole moment (Fig. 1b).23,24 Plane-polarised light is expected to be most strongly absorbed by an azobenzene-based chromophore if the direction of light polarisation coincides with the longest molecular axis.<sup>25,26</sup> These considerations indicate that a crystal structure in which the longest axes of all chromophores are aligned in parallel would also make the absorption of plane-polarised light highly dependent on the mutual orientation of the crystal and the plane of polarisation of light.<sup>27,28</sup> It is important to note that achieving a parallel alignment of chromophores in a crystal means that dichroic behaviour should be observable regardless of the crystal face that is being observed under plane polarised light.

In the context of crystal engineering with planar aromatic chromophore molecules, such as azobenzenes, the task of achieving an all-parallel orientation of chromophores is reduced to avoiding the formation of herringbone structures. This is a problem already encountered in crystal engineering, for example in the design of organic semiconductors or improving the compressibility of solid pharmaceuticals.<sup>29–34</sup> In the context of designing dichroic cocrystals, there are several means to achieve this goal (Fig. 1c and d).<sup>22</sup> One is through cocrystallisation with cocrystal formers substituted with aliphatic chains that induce parallel, lamellar-like stacking *via* interdigitation. Another one is through cocrystallisation with cocrystal formers that act as linear, ditopic linkers. Cocrystallisation with such cocrystal formers leads to the formation of one-dimensional, linear chains that exhibit a tendency for parallel stacking.<sup>22</sup>

So far, the only designs presented for crystal engineering of dichroic cocrystals have involved azobenzene chromophores acting as halogen bond donors or acceptors, coupled with suitably chosen complementary organic cocrystal

formers.<sup>22</sup> As the next step in the development of a general strategy to synthesise dichroic materials, we now address the use of metal-containing building blocks. In principle, the introduction of a transition metal ion into a design for the synthesis of a dichroic cocrystal could enable the development of novel, multifunctional materials that couple control over optical properties with magnetic, spectroscopic or other properties offered by transition metal ions. However, whereas crystal engineering by halogen bonding is overall a rapidly expanding field, the development of general strategies for cocrystallisation of metal complexes has remained modest.<sup>35</sup>

As our first entry into developing metal-containing halogen-bonded cocrystals exhibiting dichroic properties, we decided to explore 1,4-diiodoocta-fluoroazobenzene chromophore as a halogen bond donor for cocrystal formation with a salt of dicyanoaurate(I) ion,  $Au(CN)_2^-$ . It was anticipated that the very rigid, symmetrical structure would enable the dicyanoaurate ion to act as an inorganic analogue of linear ditopic halogen-bond acceptors that have previously been used in the synthesis of halogen-bonded dichroic cocrystals, such as 4,4-dipyridyl (Scheme 1a).

It is worth noting that dicyanoaurate(I) ions have already been used to achieve control over optical properties of metal-organic solids, such as luminescence emission or birefringence, through coordination-driven assembly of small molecule coordination complexes.<sup>36–38</sup> Therefore, Au(CN)<sub>2</sub><sup>-</sup> seemed as a reasonable choice of halogen bond acceptor<sup>39</sup> for our first entry into developing metalorganic designs for dichroic halogen-bonded systems. A readily commercially accessible source of  $Au(CN)_2^{-}$  is the potassium salt  $KAu(CN)_2$ . However, none of our initial attempts to synthesise a salt cocrystal involving 1,4-diiodooctafluoroazobenzene and KAu(CN)2 were successful, presumably due to the low solubility of the potassium dicyanoaurate(I) salt in most organic solvents. Consequently, we focused our efforts on cocrystallisation in the presence of 15crown-5 (15-c-5) (Scheme 1b), a crown ether agent that can enhance the solubility of KAu(CN)<sub>2</sub> in non-polar solvents through complexation with the K<sup>+</sup> ion.<sup>40</sup> Through the use of this crown ether complexation agent, we now report the formation and dichroic properties of a four-component crystalline solid (1) in which the concepts developed for the synthesis of dichroic halogen-bonded cocrystals have been successfully extended to metal-organic materials.



Scheme 1 (a) Anticipated anionic metal-organic halogen-bonding motif involving dicyanoaurate(I) anions as acceptors and molecules of 4,4'-diiodooctafluoroazobenzene as donors of halogen bonds and (b) a molecule of 15-c-5 crown ether.

# Experimental

### Synthesis

With the exception of the azobenzene halogen bond donor and chromophore, *trans*-4,4'-diiodooctafluoroazobenzene, all chemicals were obtained commercially from Sigma-Aldrich. This halogen bond donor was synthesized according to the previously reported procedure.<sup>16</sup>

Cocrystallisation was performed by solvent evaporation. In a typical experiment, 6 mg of the azobenzene (0.01 mmol) were dissolved in a minimal volume of dichloromethane (approximately 2.5 mL). After that, 3 mg of potassium dicyanoaurate (0.01 mmol) and 0.1 mL of the crown ether 15-crown-5 (**15-c-5**, 0.5 mmol) were introduced to the solution, which was then sonicated in a laboratory sonic bath until complete dissolution of dicyanoaurate. The substantial excess of **15-c-5** was deemed necessary to increase the rate of dissolution of potassium dicyanoaurate, as well as to ensure the presence of a sufficient amount of crown ether for cocrystallisation, even if a fraction of it evaporated during the procedure. The solution was left to evaporate in a vial at room temperature until almost all of the solvent had been removed. Upon evaporation, long rod-like crystals (**1**) formed, which exhibited notable dichroic properties under plane-polarised light.

Mechanochemical<sup>41</sup> milling synthesis of **1** was performed in a Retsch MM400 shaker mill operating at 30 Hz. One stainless steel ball (7 mm diameter, 1.4 gram weight) was placed in a 14 mL polytetrafluoroethylene (PTFE) jar, along with 4,4'-diiodooctafluoroazobenzene (60 mg, 0.1 mmol), potassium dicyanoaurate(I) (30 mg, 0.1 mmol) and 50  $\mu$ L **15-c-5** (2.5 equivalents, as calculated from the structure of **1** determined by single crystal X-ray diffraction). Milling was conducted for 60 minutes, after which the milling jar was opened, and sample left to dry in air at room temperature.

### X-ray powder and single crystal diffraction experiments

X-ray powder diffraction patterns were recorded on a Proto AXRD, using a 600 W CuK $\alpha$  ( $\lambda = 1.5418$  Å) radiation source and a Dectris MYTHEN 1K 1-dimensional linear detector.

Single crystal X-ray diffraction data were collected on a Bruker D8 diffractometer with an APEX2 detector using graphite-monochromatized MoKa radiation ( $\lambda = 0.71073$  Å) from a microfocus source, equipped with an Oxford Cryostream cooling system. Data collection temperature was set to 150 K, as attempts to resolve the crystal structure from room temperature data were hindered by extensive disorder of 15-c-5 moieties. Bruker APEX2 (ref. 42) software was used for data collection, while Bruker SAINT software43 was used for data integration and reduction. Semi-empirical absorption correction was applied using SADABS.44 The structure was solved using SHELXT-2014/5 (ref. 45) and refined by full-matrix least-squares using SHELXL-2016/6 (ref. 46) within the OLEX2 (ref. 47) and WinGX48 environments. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined as riding on the parent carbon atoms with  $U_{\rm H} = 1.2 \times U_{\rm C}$ . The manuscript figures were generated using MercuryCSD49 and POV-Ray50 software. Crystal structure refinement was complicated by a complex disorder of the  $[K(15-c-5)_2]^+$  cation. Careful examination of the electron density maxima at a reasonable distance from

the potassium cation and from each other revealed the oxygen atoms belonging to 15-c-5. Next, the carbon atoms of 15-c-5 could be identified in the differential electron density map, and the gradual introduction of restraints for 1,2- and 1,3distances and subsequent refinement allowed the modelling of one disorder component of the  $[K(15-c-5)_2]^+$  cation. The second component was modelled in a similar fashion from the residual electron density. Finally, the disorder was modelled over two components, with restraints on the 1,2- and 1,3-distances and the anisotropic displacement parameters in the 15-c-5 molecules. Their respective occupancies were freely refined, both converging to 0.500(3). Next, the structure was found to contain another, non-complexed 15-c-5 molecule, disordered around an inversion center. It was modelled similarly to the 15-c-5 in the [K(15-c- $5_{2}^{1+}$  cation, with restraints applied to 1,2- and 1,3-distances as well as the anisotropic displacement parameters, with the occupancy fixed to 0.5. Rigid bond restraints were applied to all the atoms in the octafluoro-4,4'-diiodoazobenzene halogen bond donor. CCDC-1539033 contains the supplementary crystallographic data for this paper.

### Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a sample of **1** simultaneously using a Mettler-Toledo TGA/DSC **1** Star system thermobalance. The samples were placed in alumina crucibles and measurements conducted in a stream of air or nitrogen (50 cm<sup>3</sup> min<sup>-1</sup>) gas, at a heating rate of 10 °C min<sup>-1</sup>. Results were processed with the Mettler STARe 9.01 software. The outcomes of the measurements are provided in the ESI.<sup>†</sup>

Hot stage microscopy was performed using a Mettler Toledo FP90 Central Processor, equipped with a Mettler FP84 HT TA Microscopy Cell. Video and images were obtained on an Infinity 1 Lumenera camera attached to a Leica DM2500 optical microscope, using the Studio Capture software suite. Heating was performed from 30 °C to 200 °C at a rate of 5 °C min<sup>-1</sup>.

### **Dichroism studies**

Dichroism measurements on crystals of **1** were conducted on a Nikon Eclipse LV100POL microscope, equipped with a Nikon DS-Fi1 camera and Nikon Digital Sight controller. Transmitted light intensity measurements were performed and analysed with the aid of the NIS-Elements BR 2.30 software suite.

### **Results and discussion**

### Structural analysis of 1

Analysis of the obtained four-component crystals of **1** *via* single crystal X-ray diffraction revealed a triclinic unit cell belonging to the triclinic space group *P*-1. General and crystallographic data for **1** are given in Table **1**. The asymmetric unit of the crystals was found to consist of a single molecule of *trans*-4,4'-diio-dooctafluoroazobenzene, one complete dicyanoaurate(I) ion, and a single potassium cation. Importantly, structural analysis revealed that the halogenated *trans*-azobenzene chromophore molecules and Au(CN)<sub>2</sub><sup>-</sup> ions assembled into the expected halogen-bonded chains held together by relatively short I···N contacts,

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$C_{39}H_{50}AuF_8I_2KN_4O_{12.50}$	Space group	<i>P</i> -1
1416.69	Z	2
150(2) K	$\rho_{\rm calc} ({\rm g}~{\rm cm}^{-3})$	1.895
0.71073 Å	$\mu (\mathrm{mm}^{-1})$	4.382
Triclinic	F(000)	1376
a = 9.0480(6)	Crystal size (mm <sup>3</sup> )	0.53 imes 0.20 imes 0.16
b = 15.1904(10)	$2\theta$ range (°)	2.25 to 54.97
c = 19.1737(12)	Data/restraints/	11 173/1912/949
	parameters	
$\alpha = 73.9435(8)$	S	1.059
$\beta = 78.7765(8)$	$R_1$ , w $R_2$ for $I > 2\sigma(I)$	0.0420, 0.1037
$\gamma = 88.9763(8)$	$R_1$ , w $R_2$ for all data	0.0591, 0.1151
2482.2(3)	$\Delta e \ \text{\AA}^{-3}$ , min, max	-0.964, 1.202
	$\begin{array}{l} C_{39}H_{50}AuF_8I_2KN_4O_{12.50}\\ 1416.69\\ 150(2)\ K\\ 0.71073\ Å\\ Triclinic\\ a=9.0480(6)\\ b=15.1904(10)\\ c=19.1737(12)\\ \\ \alpha=73.9435(8)\\ \beta=78.7765(8)\\ \gamma=88.9763(8)\\ 2482.2(3)\\ \end{array}$	$\begin{array}{ll} C_{39}H_{50}{\rm AuF}_{8}I_{2}{\rm KN}_{4}O_{12.50} & {\rm Space\ group} \\ 1416.69 & Z \\ 150(2)\ {\rm K} & \rho_{\rm calc}\ ({\rm g\ cm}^{-3}) \\ 0.71073\ {\rm \mathring{A}} & \mu\ ({\rm mm}^{-1}) \\ {\rm Triclinic} & F(000) \\ a = 9.0480(6) & {\rm Crystal\ size\ ({\rm mm}^{3})} \\ b = 15.1904(10) & 2\theta\ {\rm range\ (}^{\circ}) \\ c = 19.1737(12) & {\rm Data/restraints/} \\ {\rm parameters} \\ \alpha = 73.9435(8) & S \\ \beta = 78.7765(8) & R_{1}, wR_{2}\ {\rm for\ } I > 2\sigma(I) \\ \gamma = 88.9763(8) & R_{1}, wR_{2}\ {\rm for\ all\ data} \\ 2482.2(3) & \Delta e\ {\rm \mathring{A}}^{-3}, {\rm min,\ max} \end{array}$

Table 1 General and crystallographic data for 1

extending along the crystallographic direction [011]. Each Au(CN)<sub>2</sub><sup>-</sup> ion was found to be involved in two distinct halogen bonds, characterised by significantly different I····N distances of 2.846 Å and 2.960 Å (Fig. 2a). Given that the sum of the van der Waals radii of nitrogen and iodine is 3.53 Å, the reduced distance parameter (*R*) for these two halogen bonds is 0.806 and 0.839, respectively. The differences in halogen bond lengths are also accompanied by expected differences in linearity. The shorter halogen bond exhibited an C-I···N angle of 177°, while the 0.1 Å longer one was more bent, at a corresponding angle of 175°.



Fig. 2 (a) View of a single anionic metal–organic halogen-bonded chain in the crystal of 1, with indicated lengths of halogen-bonded distances around the dicyanoaurate(I) acceptor and (b) view of the crystal structure 1 with regions of positive electron density (shown in green) indicating the presence of 15-c-5 molecules that are either closely associated with potassium ions to form complex [K(15-c-5)]<sup>+</sup> cations, or located between the [K(15-c-5)]<sup>+</sup> moieties.

Besides the anionic halogen-bonded chains and potassium counterions, the analysis of the difference electron density map revealed the presence of additional three crystallographically non-equivalent 15-crown-5 molecules in the asymmetric unit of **1**. Of these, two were found situated in the close vicinity of the  $K^+$  ion, consistent with the formation of the previously<sup>40</sup> observed  $[K(15-c-5)_2]^+$  species. The third type of **15-c-5** molecule was found to be disordered around a crystallographic inversion centre, sandwiched between two  $[K(15-c-5)_2]^+$  moieties (Fig. 2b and 3a). The difficulty in resolving the atom positions of the **15-c-5** molecules was interpreted as a result of considerable thermal motion, further buttressed by thermal elliposids being considerably larger than those associated with metal-



Fig. 3 (a) An ORTEP representation of the contents of the asymmetric unit of 1, with hydrogen atoms omitted for clarity. The  $Au(CN)_2^-$  and azobenzene moieties in the asymmetric unit belong to different halogen-bonded chains. All atoms are shown at 30% ellipsoid probability level, and the disorder of 15-c-5 and  $[K(15-c-5)_2]^+$  moieties is not shown for clarity. (b) Views of the crystal structure of 1 approximately parallel to the crystallographic *a*-axis, revealing the assembly of halogen-bonded anionic metal–organic chains separated by  $[K(15-c-5)_2]^+$  cations and 15-c-5 solvent molecules (shown in space filling, gray and white, respectively).

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organic halogen-bonded chains even when data collection was performed at 150 K.

The crystal structure of **1** (Fig. 4b) is particularly interesting from the standpoint of crystal engineering, as the presence of discrete **15-c-5** molecules in the crystal structure makes **1** an interesting example of a solid that combines the definitions of several types of multi-component crystals: it is a cocrystal by virtue of directed halogen-bonded assembly of the neutral *trans*-azobenzene chromophores with Au(CN)<sub>2</sub><sup>-</sup>. It also conforms to the definition of a true salt, through the combination of  $[K(15-c-5)_2]^+$  and Au(CN)<sub>2</sub><sup>-</sup> ionic species. And, finally, the inclusion of discrete units of **15-c-5**, which on its own is a liquid under ambient condition, make **1** also fit the definition of a solvate.

Besides crystallisation from solution, we also explored an alternative route for the synthesis of 1, by mechanochemical<sup>41</sup> ball milling. In particular, after the composition of 1 was established with the aid of single crystal structure determination, we attempted its one-step multi-component mechanochemical synthesis through milling of equimolar amounts of KAu(CN)<sub>2</sub> and the transazobenzene halogen bond donor with 2.5 equivalents of the liquid reactant 15-c-5. After 60 minutes of milling, the powder X-ray diffraction (PXRD) analysis of the resulting orange powder revealed X-ray diffraction signals that were largely, but not completely, consistent with those measured for solution-grown crystals of 1 or calculated from the crystal structure of 1 (Fig. 4). Importantly, the mechanochemically prepared sample exhibited additional broad X-ray reflections that could not be reconciled with those expected for 1, most notably at  $2\theta$  angles of 18.1 °C and 21.5 °C. Whereas these reflections do not correspond to any of the starting materials, we find that they appear upon neat milling of  $KAu(CN)_2$ , indicating that this reactant undergoes a competing solid-state transformation upon milling (Fig. 4). Differences were also observable between the PXRD patterns measured for crushed single crystals of 1 and simulated from its crystal structure.



Fig. 4 Overlay of selected PXRD patterns (from top to bottom): pattern simulated for the herein reported crystal structure of 1; measured pattern for gently crushed crystals of 1 grown from solution; the product of mechanochemical reaction of KAu(CN)<sub>2</sub>, **15-c-5** and 4,4'-diiodotetrafluoroazobenzene; KAu(CN)<sub>2</sub> after 30 minutes milling; KAu(CN)<sub>2</sub> starting material and solid 4,4'-diiodotetrafluoroazobenzene reactant.

These differences can be rationalised by preferred orientation in the solutiongrown sample, which could affect reflection intensity, and a mismatch between the temperature of PXRD measurement compared to single crystal X-ray diffraction data collection (150 K). The difference in temperature could lead to a shift in reflection angles and, which is less likely in this case, change in crystallographic parameters and symmetry.<sup>51,52</sup>

### Infrared spectroscopy

Fourier-transform infrared attenuated total reflectance (FTIR-ATR) measurements were performed on a Bruker VERTEX 70 instrument equipped with a PLATINUM diamond crystal ATR unit. The comparison of FTIR-ATR spectra for crystals of **1** grown from solution to the product of the milling reaction, as well as individual solid reactants is provided in Fig. 5. The infrared spectra clearly demonstrate the presence of cyanide ion stretching bands in samples obtained from solution and by milling.

### Thermal analysis

Simultaneous TGA/DSC analysis of **1** in either nitrogen gas or air (see ESI<sup>†</sup>) revealed that thermal degradation happens in a single thermal decomposition step above 100 °C. The decomposition is characterised by a *ca.* 75% weight loss (Fig. 6a), which is reasonably close to that expected for the loss of all **15-c-5** and 4,4'-diiodooctafluoroazobenzene contained in **1** (evaluated at 79.6%). This suggests that the thermal decomposition of **1** leads to complete degradation into residual KAu(CN)<sub>2</sub>. This is also supported by hot-stage microscopy, that revealed degradation of **1** above 100 °C, recognized by the loss of transparency of crystals, and the formation of a colourless solid residue close to 200 °C (Fig. 6b–d).



Fig. 5 Overlay of selected FTIR-ATR spectra (top to bottom): crystals of 1 obtained from solution; milling reaction; 4,4'-diiodotetrafluoroazobenzene and solid KAu(CN)<sub>2</sub> reactant.



Fig. 6 Selected thermal analysis data for crystals of 1: (a) TGA thermogram for 1, recorded in a dynamic atmosphere of nitrogen gas. The expected combined weight loss for all 4,4'- diiodooctafluoroazobenzene and 15-c-5 contained in 1 is 79.7%, and the experimentally obtained value of 74.7% indicates that thermal decomposition of 1 leads to complete loss of these components. Snapshots of thermal degradation of 1 obtained through hot-stage microscopy in air, taken at: (b) 49.4 °C; (c) 119.0 °C and (d) 194.8 °C.

### Dichroism of single crystals of 1

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All single crystals of **1** were found to exhibit rod-like habits, with two dominant sets of faces. For the herein studied crystals, typical crystal thickness was *ca.* 200  $\mu$ m and indexing of several single crystals revealed that the largest face of the crystal corresponds to the (011) set of faces (see ESI† for indexing image of a crystal following crystallographic unit cell determination). Inspection under a polarised microscope revealed a noticeable dichroic effect for the (011) face, as the colour of the single crystals was found to change from red to colourless twice upon rotation of the crystal over 360° (Fig. 7a–c).

Importantly, however, the dichroic properties of the crystals were not limited to the (011) set of faces, as was demonstrated by apparent changes in colour of the crystal when oriented parallel to the other significant pair of faces, which was determined to correspond to the (001) set of crystal planes (Fig. 8a and b). Also in this case, the crystal changed colour from red to colourless two times during a full 360° rotation in the plane of the polariser (Fig. 8c). Other crystal faces were too small to readily investigate their dichroic behaviour.

The described dichroic properties of crystals of **1** can be readily explained by examining the structure of crystal planes parallel to the (011) and (001) set of crystal faces, as in both cases the crystal planes exhibit a parallel alignment of the azobenzene chromophore molecules. The (011) crystal planes are coplanar with the direction of propagation of the halogen-bonded chains, and this set of planes consists of consecutive anionic layers containing halogen-bonded metal–organic chains, sandwiched between cationic layers consisting of  $[K(15-c-5)_2]^+$  moieties surrounded by **15-c-5** molecules (Fig. 7d and e). Importantly, in each anionic layer all azobenzene chromophores are aligned in parallel, explaining the observed dichroism. The (001) family of crystal planes contains both cationic and anionic components (Fig. 8d), and intersects the metal–organic halogen-bonded chains at



**Fig. 7** Dichroism of the (011) crystal face for a single crystal of **1**: (a) and (b) polarization microscope images of the (011) crystal face at different orientations of a crystal of **1** with respect to the polariser. (c) Changes in the intensity of polarised light transmitted normal to the (011) set of faces of a crystal of **1**, depending on the orientation of the crystal. Two different views of the assembly of azobenzene chromophore (red) and Au(CN)<sub>2</sub><sup>-</sup> ions (blue) in a layer parallel to the set of crystallographic (011) planes: (d) as seen along the crystallographic *a*-axis, and (e) as seen approximately parallel to the plane, respectively. The orientation of the (011) crystal plane is illustrated by the blue rectangle.

an angle of *ca.* 48°. Nevertheless, when viewed along the crystallographic *c*-axis all azobenzene chromophores are aligned in parallel, consistent with the observed dichroic behaviour.





**Fig. 8** Dichroism of the (001) crystal face for a single crystal of **1**: (a) and (b) polarization microscope images of the (001) crystal face at different orientations of the crystal with respect to the polariser. (c) Changes in the intensity of polarised light transmitted normal to the (001) set of faces of a crystal of **1**, depending on the orientation of the crystal. (d) View of the contents of the crystallographic (001) plane viewed along the crystallographic *c*-axis, with  $[K(15-c-5)_2]^+$  and discrete **15-c-5** molecules shown using a space-filling model, the azobenzene chromophores shown in red and  $Au(CN)_2^-$  ions in blue.

# Conclusion

This work provides a proof-of-principle demonstration that the halogen-bonding cocrystallisation strategy developed to facilitate the formation of dichroic structures based on organic molecules,<sup>22</sup> can also be applied to metal-organic materials. In particular, we have demonstrated the assembly of azobenzene chromophores into linear metal-organic chains by halogen bonding to rigid

ditopic dicyanoaurate(I) acceptors. Similar to our previous report on organic cocrystals,<sup>22</sup> in this case also the parallel assembly of halogen-bonded chains leads to a crystal structure in which all chromophores are aligned, resulting in dichroism. Importantly, the herein presented structure of **1** also shows that the design principle used to generate dichroic molecular solids are also applicable to ionic materials. The structure of **1** is also of intrinsic interest in the context of crystal engineering, as its four-component composition makes it simultaneously conform to definitions of a molecular cocrystal, salt and a solvate. We believe that the structure and properties of **1** provide an important and useful step forward in utilising halogen bonding for the further design of multi-component and potentially multi-functional metal–organic materials with interesting optical properties.

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