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Characteristic redshift and intensity enhancement as Far-IR fingerprints of the halogen bond involving aromatic donors†

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Six halogen-bonded cocrystals involving aromatic donors have been studied by far-IR spectroscopy. Characteristic redshift and intensity increase of the C-I stretching band have been observed, which provided a distinct signature of the halogen bond involving iodopentafluorobenzene.

In the late sixties, a number of spectroscopic studies in the far-infrared (IR) region have regarded halogen-bonded complexes involving strong donors, such as I_2[1] and ICl,[2] and various acceptors. These studies highlighted several common features such a red-shift and an enhancement of the IR absorption bands of the covalent bonds the halogen-bond donor sites were involved in.[3] These features were indicative of the charge-transfer component of the interaction and connected with the charge flux from the electron-donor to the acceptor partner.[4-6] Similar features were also observed when aliphatic iodoperfluorocarbons were used, e.g., CF_3I.[7-9]
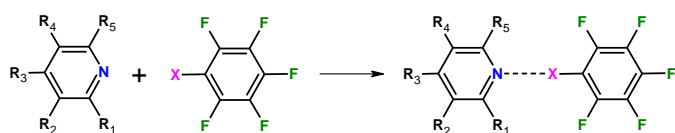
1 $R_1 = R_2 = R_3 = R_4 = R_5 = H; X = I$
2 $R_2 = CH_3; R_1 = R_3 = R_4 = R_5 = H; X = I$
3 $R_3 = CH_3; R_1 = R_2 = R_4 = R_5 = H; X = I$
4 $R_2 = R_4 = CH_3; R_1 = R_3 = R_5 = H; X = I$
5 $R_1 = R_2 = R_3 = R_4 = R_5 = H; X = Br$

6
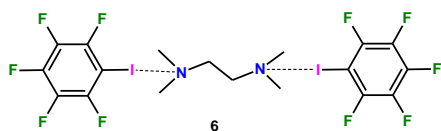
Scheme 1. The synthesized dimeric, **1-5**, and trimeric, **6**, halogen-bonded cocrystals.

Various halogen-bonded complexes involving the different trifluoromethyl halides and formed in cryo-matrices were more recently investigated in detail by using IR and Raman spectroscopies.[10-12] However, to the best of our knowledge, no study has regarded, so far, the far-IR investigation of halogen-bonded complexes involving haloperfluoroaromatic donors despite they are common and effective halogen-bond donor sites, frequently present also in molecular materials endowed with unique and useful properties.[13]

The performance of a halogen-bond donor largely depends on the degree of polarization of the halogen atom, i.e., the greater the positive electrostatic potential of the σ-hole, the more effective the halogen-bond donor will be.[14] This means that the magnitude of the positive potential of the σ-hole depends on the ability of the halogen atom to be polarized, as well as on the presence of electron-withdrawing moieties that cause a depletion of electron density on the halogen atom. In this respect, iodoperfluoroaromatics are very good halogen-bond donors, tough weaker than I_2 and iodoalkynes.[15]

On the other hand, iodopentafluorobenzene easily undergoes selective nucleophilic substitution at its para-positioned fluorine atom, allowing high-yield introduction of halogen-bond donor tectons on various molecular platforms.[16] This prompted us to study the far-IR features of the C-X bond (X = Br and I) in model halogen-bonded complexes involving haloperfluoroaromatics in order to ascertain the fingerprint of the occurrence of the halogen bond.

In this paper we report an experimental and theoretical far-IR study of six prototypical halogen-bonded cocrystals, which were also fully characterized by single crystal and powder X-ray crystallography and calorimetry. Very simple starting tectons were chosen to be devoid of functional groups that could interfere with the occurrence of the halogen bonds or modify its features. Monodentate halogen-

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bond donors such as iodopentafluorobenzene (IPFB) and bromopentafluorobenzene (BrPFB) were chosen in order to obtain dimeric and trimeric adducts with minimal crystal packing requirements with respect to those of multimeric adducts or the infinite chains formed by dihalotetrafluorobenzenes. As far as the halogen-bond acceptors are concerned, pyridine, 3-methylpyridine, 4-methylpyridine, and 3,5-dimethylpyridine, were chosen, along with tetramethylethylenediamine as an example of aliphatic acceptor (Scheme 1). Single crystal X-ray structures of the obtained adducts **1-6** confirmed that the X···N halogen bonds (X= I, Br) were, by far, the most important interactions in the crystals. Other interactions being relatively long, namely weak, the studied IR characteristics are indicative of the inherent features of the halogen bonds rather than of halogen bonds heavily perturbed by crystal packing effects.
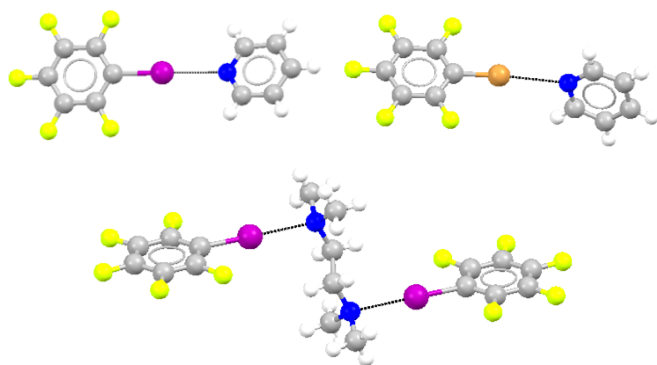
Figure 1. Halogen-bonded dimers in the crystal structures of **1** (top, left) and **5** (top, right), and trimer in **6** (bottom). Colours are as follows: C, grey; H, light grey; N, blue; F, yellow; Br, orange; I, magenta. Black dotted lines are the N···I and N···Br halogen bonds.

The six halogen-bonded cocrystals were synthesized by direct mixing of the liquid starting materials in either 1:1 (**1**, **2**, **3**, **4**, and **5**) and 1:2 (**6**) molar ratios, taking into account the pairing of the respective halogen bond donor and acceptor sites. Crystallization of **2-4** and **6** occurred during blending, while **1** and **5** remained liquids at room temperature. The formation of new, discrete adducts and the absence of remaining starting compounds were confirmed by differential scanning calorimetry (DSC) measurements. New single melting and crystallization peaks were obtained, which differed from the starting compounds. In particular, while all starting compounds melted at temperatures below 0 °C (from -60 to -6 °C), all of the iodinated cocrystals melted well above 0 °C, from +18 to +53 °C. Cocrystal **5**, instead, melted at -22 °C, which finds justification in the lower strength of the halogen bond given by BrPFB[14] (for further details please see Table S1 in the ESI).

The structures of the obtained halogen-bonded cocrystals were determined *via* single crystal X-ray diffraction analysis. Cocrystals **1**

(m.p.: +18 °C) and **5** (m.p.: -22 °C) were generated and analysed in situ by means of an optical heating and crystallization device (OHCD),[7] in order to obtain single crystals suitable for X-ray diffraction.

The structures of cocrystals **3** and **4** were already reported in the Cambridge Structural Database[8] (Refcodes: LEZQAJ and LEZPUC, LEZPUC01, respectively).[9] The structures of both polymorphs of **4** (LEZPUC, LEZPUC01) were obtained at 298 K and 150 K, respectively. All other cocrystals' structures have never been reported before. Expectedly, the self-assembly of the starting compounds into dimers **1-5** and trimer **6** is driven by short X···N (X = I, Br) contacts, see Figure 2. The I···N distance is in the range 2.728(2) – 2.841(9) Å, corresponding roughly to a 20% reduction of the sum of the vdW radii for I and N (3.50 Å).[20] The Br···N distance found in **5** was 2.882(2) Å, which corresponds to a 15% reduction of the sum of the vdW radii for Br and N (3.40 Å).[20] All crystal structures adopt monoclinic P21/c or P21/n space groups showing strong similarities in their packing.

Once ascertained the occurrence of the halogen bond in all of the obtained cocrystals, these were submitted to IR spectroscopy studies, in particular in the far-IR region at room temperature, in order to determine how halogen bond affects vibrations of the involved molecular components. However, due to the limited literature on the topic, it was essential to first accurately assign the molecular vibration bands by calculations and then possibly predict the ones that should manifest a detectable change upon formation of the halogen bond. Therefore, we carried out a detailed vibrational analysis in the gas phase by density functional theory (DFT) calculations starting from the optimized geometry observed in the above described structures (see Table 1 and Section S.5 of the ESI for the detailed methodology).

Four vibrations of IPFB were located in the far-IR region, those being out-of-plane C-I bending at 80 cm^{-1}, in-plane C-I bending at 132 cm^{-1}, and in-plane C-I stretching at 204 cm^{-1}, plus ring wagging at 212 cm^{-1}. The latter three are in a very good agreement with the experimental ATR-FTIR spectroscopic measurements (132 cm^{-1}, 204 cm^{-1} and 214 cm^{-1}), whereas the out-of-plane C-I bending, unfortunately, falls just outside our experimental range. Furthermore, the DFT calculations showed that a noticeable shift of the afore-mentioned vibrational modes should occur upon involvement of IPFB in halogen bond. In fact, a redshift of around 15 cm^{-1} was calculated for the C-I stretching vibration, whereas the C-I bending mode was shown to shift to higher wavenumbers (blueshift) by approximately the same amount.

Indeed, we observed clear shifts in the far-IR region of the experimental spectra of the cocrystals involving IPFB, *i.e.*, **1-4** and **6** (Table 1). In particular, the in-plane C-I stretching vibration of pure IPFB shifted from 204 cm^{-1} to 193 cm^{-1} in **1** and up to 188 cm^{-1} in **2** and **6** (Fig. 2). A similar redshift was previously reported by N. F. Cheetham and A. D. E. Pullin for the complex between trimethylamine and CF$_3$I.[7]

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Table 1 Experimental (Exp.) and calculated (Calc.) values of selected far-IR vibration bands associated to the C-X bond in pure compounds and related cocrystals. Calculated intensity increase is the ratio between the C-X stretching band and the C-F out of plane wagging mode in both the cocrystal and the pure compound (see Section S.5 in the ESI). For the calculation of the experimental intensity increase, please see Section S.4 in the ESI.

Compound /cocrystal	In plane C_6F_5-X bending (cm^{-1})		In plane C_6F_5-X stretching (cm^{-1})			
	Exp	Calc.	Exp.	Calc.	ΔI^a (%)	ΔI^b (%)
IPFB	132	132	203	204	-	-
BrPFB	155	155	242	243	-	-
1	140	151	193	192	7	28
2	146	147	188	191	36	51
3	143	148	192	191	41,5	59
4	143	146	191	190	25	33
5	155	168	241	236	0	0
6	*	139	188	189	21	7

^{a} Calculated intensity increase; ^{b} Experimental intensity increase;
* Too low intensity to be detected.

The observed redshift is perfectly consistent with the weakening and lengthening of the C-I bond[21] upon halogen bonding the pyridine nitrogen.[22] Alongside the above-discussed shift, we also observed a remarkable intensity increase of the same vibration band of IPFB when involved in cocrystals, see Figure 2. This intensity increase was also reproduced by DFT calculations (Table 1) and may find an explanation in the intrinsic charge transfer characteristics of the halogen bond.[1-9] In fact, according to Torii *et al.*[23] intensity increase of IR vibrations occurs in halogen bonded cocrystals as a consequence of the intermolecular charge flux from the electron donor to the acceptor counterpart, thus affecting the dipole moment derivative of the C-I stretching mode. This leads to an increase of IR intensity,[21] since this latter is proportional to the square of the dipole moment derivative with respect to the normal mode of vibration.

Also the C-I bending vibration of IPFB experienced a characteristic change, undergoing a blueshift of *ca.* 10 cm^{-1} in co-crystals **1-4**, and **6**. However, no intensity variations were either predicted or observed for this specific vibration.

On the other hand, cocrystal **5**, the only one containing bromine as a halogen bond donor site, showed neither appreciable C-Br band shift nor intensity increase. The slightly worse agreement between gas phase calculated and solid-state measured wavenumbers (Table 1) in **5** is probably due to the different constrains in the solid state. The smaller dimensions of Br, in fact, allows for a better packing, increasing the differences between the solid state and the gas phase IR frequencies, due to interactions with the neighbouring atoms.

Clearly, iodine causes changes in IR spectra of corresponding complexes greater than those of bromine, this difference being related to the more positive σ hole on IPFB compared to BrPFB.[25] Higher polarizabilty of iodine compared to bromine enhances the electropositive cap on the electrostatic potential surface of the halogen atom allowing for the occurrence of stronger intermolecular

interactions.[26] This is consistent with a general trend of the halogen bond strength, which decreases in the order I > Br > Cl.[27]

All of the above discussed findings prove the successful formation of charge transfer complexes driven by the I⋯N halogen bond. However, neither I⋯N nor Br⋯N vibration bands were detected in our experimental set up, which might be due to either the band residing out of the range measured (*i.e.*, <100 cm^{-1}) or its intensity being too weak to be detected, both hypotheses being in line with recently calculated interaction vibrations.[8]
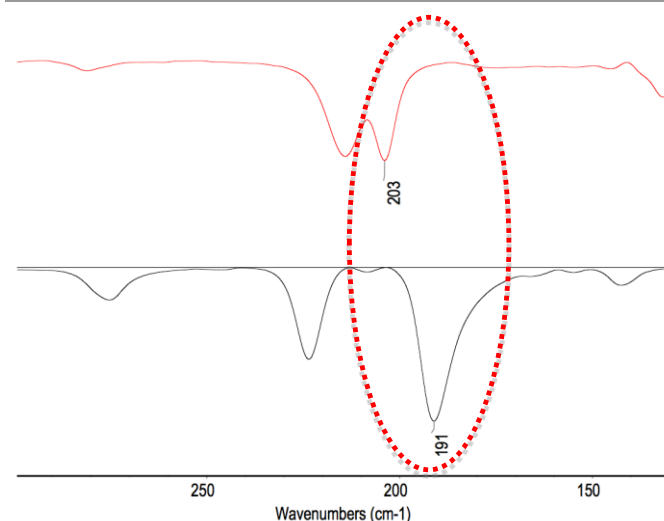
Figure 2. Normalized far-IR spectra of **IPFB** (red, top) and related co-crystal **4** (black, bottom). A clear redshift of *ca.* 12 cm^{-1} and an intensity increase of about 25% was observed for the in plane C-I stretching band upon occurrence of the halogen bond (red dashed line).

In summary, six cocrystals assembled through halogen bond were fully characterized *via* XRD, DSC, and IR analyses. C-X (X = Br and I) normal modes of vibration of haloperfluoroaromatic donors C_6F_5X, directly involved in the intermolecular halogen bond, were assigned by both experimental analysis and ab initio theoretical calculations for all of the studied cocrystals. We have demonstrated that the C-I vibration band undergoes a clear redshift and intensity increase upon occurrence of the halogen bond. This new spectroscopic fingerprint of the halogen bond involving iodoperfluoroaromatics may develop as a routine tool to detect its occurrence in materials[28] when alternative methods are not available. This is clearly the case of amorphous materials, polymers,[29,30] liquid crystals, and fibrils[31] where more complex and advanced methods, such as Raman spectroscopy[32] and X-ray Photoelectron Spectroscopy (XPS)[33] have been used. Thanks to the availability of the modern instruments at reasonable cost, far-IR spectroscopy may nowadays develop as a powerful and sensitive technique for the fast and easy study of intermolecular interactions. IR spectroscopy typically allows for the halogen bond formation to be detected in the solid state *via* the blueshift and intensity decrease of the C-H stretchings shown by the halogen-bond pyridine acceptors or the red shift of the C-F stretchings shown by iodoperfluoroalkanes (see Section S.4 in the ESI).[21] The new fingerprint here reported complements these possibilities and affords the first vibrational tool to detect the direct

occurrence of the interaction *via* changes in the IR features of iodoperfluoroaromatics, common moieties in halogen bonded molecular materials.

Furthermore, the present study also contributes to the ongoing discussion on the nature of the halogen bond demonstrating a charge-transfer contribution in the studied systems evidenced by the band intensity increase associated to the C–I bond. A more systematic study is currently undergoing in our laboratories to ascertain the generality of the findings described in this paper, by also studying a series of complexes involving iodoperfluoroalkanes, a well-known class of halogen bond tectons. These fuller results will be reported elsewhere.

Notes and references

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Characteristic redshift and intensity enhancement of the C-I stretching band have been proven to be distinct signatures of the halogen bond involving iodopentafluorobenzene.