

## An accurate vibrational signature in halogen bonded molecular crystals

### Figures

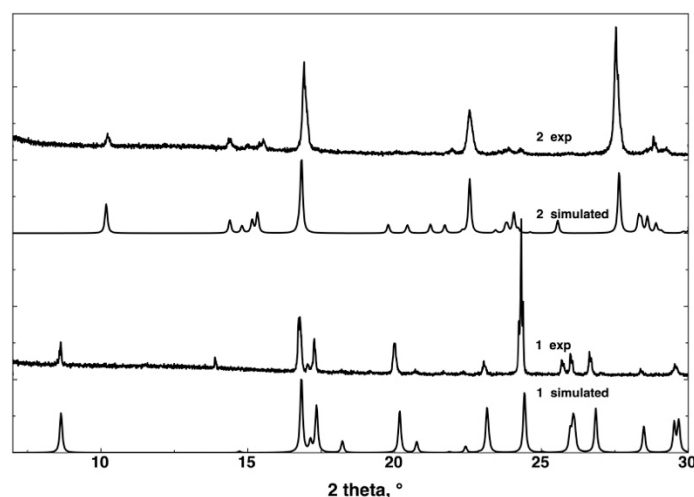


Figure S1: PXRD diagram simulated and experimental for the 1D structure of **1**<sup>1</sup> and **2**.<sup>2</sup>

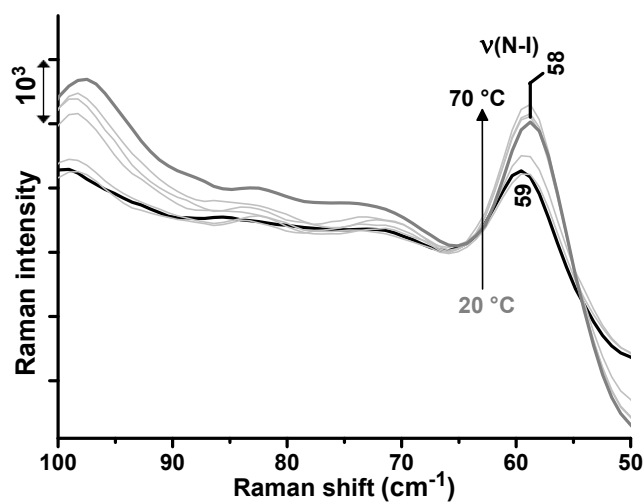


Figure S2: Temperature dependence of the halogen bonding band of **1** from 20 to 70 °C. This enlarged view of the spectral range from 100 to 50 cm<sup>-1</sup> shows the  $\nu(\text{N-I})$  vibrational mode corresponding to the band in Raman spectrum of **1** in Figure 2A.

1 D. Cinčić, T. Friščić, W. Jones, Isostructural Materials Achieved by Using Structurally Equivalent Donors and Acceptors in Halogen-Bonded Cocrystals. *Chem. Eur. J.* **2008**, *14*, 747-753.

2 P. Ravat, S. Seetha Lekshmi, S. N. Biswas, P. Nandy, S. Varughese, Equivalence of Ethylene and Azo-Bridges in the Modular Design of Molecular Complexes: Role of Weak Interactions. *Cryst. Growth Des.* **2015**, *15*, 2389-2401.

## Crystallographic data

	<b>1<sup>1</sup></b>	<b>1</b>	<b>2<sup>2</sup></b>
CCDC N <sup>o</sup>	649670	2169122 <sup>a</sup>	742922
CCDC Refcode	DIVCUH		BULKEA
Empirical formula	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> , C <sub>6</sub> F <sub>4</sub> I <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> , C <sub>6</sub> F <sub>4</sub> I <sub>2</sub>	C <sub>10</sub> H <sub>8</sub> N <sub>4</sub> , C <sub>6</sub> F <sub>4</sub> I <sub>2</sub>
Formula weight	488.00	488.00	586.06
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	5.2777(2)	5.2774(2)	6.414(4)
<i>b</i> /Å	6.0948(2)	6.0924(2)	8.358(5)
<i>c</i> /Å	10.3019(3)	10.3058(4)	9.202(6)
$\alpha$ /°	90.851(2)	90.853(2)	82.982(9)
$\beta$ /°	96.934(2)	96.872(2)	70.979(9)
$\gamma$ /°	99.1130(10)	99.081(2) <sup>o</sup>	78.678(9)
Volume/Å <sup>3</sup>	324.605(19)	324.66(2)	456.4(5)
<i>Z</i>	1	1	1
$\rho_{\text{calc}}$ /cm <sup>3</sup>	2.496	2.496	2.132
$\mu$ /mm <sup>-1</sup>	4.876	4.875	3.491
F(000)	226	226	274
Color	colorless	colorless	orange
T(K)	180(2)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	180	100	100
2 $\theta$ range for data collection/°	1.99 to 33.66	3.39 to 30.17	2.35 to 25.56
Reflections collected	2551	1722	1665
Independent reflections	2309	1722	1584
Goodness-of-fit on F <sup>2</sup>	1.175	1.108	1.040
Final R indexes [ <i>I</i> >= 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0298, wR <sub>2</sub> = 0.0758	R1 = 0.0172, wR2 = 0.0448	R <sub>1</sub> = 0.0353, wR <sub>2</sub> = 0.0946
Final R indexes [all data]	R <sub>1</sub> = 0.0375, wR <sub>2</sub> = 0.0939	R1 = 0.0176, wR2 = 0.0452	R <sub>1</sub> = 0.0368, wR <sub>2</sub> = 0.0964
Largest diff. peak/hole / e Å <sup>-3</sup>	1.104/-2.277	0.819 / -0.758	1.433/-0.933

**Table S1.** Crystallographic data for **1** and **2** measured at 180 K and 100K respectively. <sup>a</sup> This compound was measured at T = 100K, for comparison with **2**, that was also measured at 100K. **1** was already measured at T = 180K.

## DFT simulation

	TFIB..Piperazine	TFIB..(Piperazine) <sub>2</sub>	TFIB..Azopyridine	TFIB..(Azopyridine) <sub>2</sub>
<b>TFIB</b>				
$r_{CF}$				
PBE0	1.325	1.330	1.332	1.330
PBE0-GD3	1.325	1.331	1.331	1.329
M06	1.322	1.315	1.328	1.326
$r_{CI}$				
PBE0	2.090	2.128	2.125	2.113
PBE0-GD3	2.092	2.132	2.129	2.117
M06	2.095	2.129	2.127	2.118
$\theta_{ICC}$				
PBE0	120.5	120.7	121.1	121.0
PBE0-GD3	120.6	120.9	121.0	120.9
M06	120.6	121.1	121.0	120.9
<b>Piperazine</b>				
$R_{NH}$				
PBE0	1.012	1.014	1.013	
PBE0-GD3	1.012	1.014	1.013	
M06	1.014	1.016	1.015	
$r_{CN}$				
PBE0	1.455	1.463	1.462	
PBE0-GD3	1.455	1.463	1.462	
M06	1.454	1.462	1.461	
$\theta_{CNC}$				
PBE0	111.1	111.7	111.7	
PBE0-GD3	111.1	111.9	111.9	

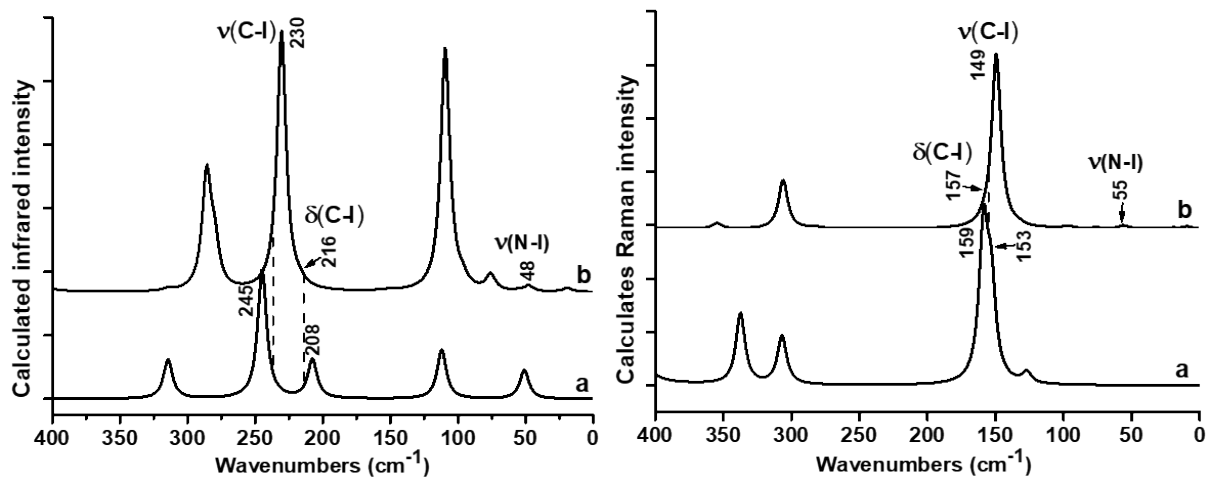
M06	111.1	112.0	112.0	
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Azopyridine				
$r_{\text{CN}}$				
PBE0	1.330		1.330	1.330
PBE0-GD3	1.330		1.330	1.335
M06	1.328		1.334	1.334
$\theta_{\text{CNC}}$				
PBE0	117.2		118.1	118.1
PBE0-GD3	117.2		118.3	118.3
M06	117.4		118.4	118.4
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Intermolecular				
$R_{\text{I}\dots\text{N}}$				
PBE0	2.836	2.866 (3.69)	2.884 (3.69)	2.913 (3.69)
PBE0-GD3	2.810	2.837 (3.69)	2.856 (3.69)	2.882
M06	2.839	2.864 (3.69)	2.862 (3.69)	2.884
$\theta_{\text{INC}}$				
PBE0	175.9	175.9	178.5	178.9
PBE0-GD3	177.5	177.2	180.0	180.0
M06	176.8	176.7	179.9	179.7
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The values in brackets are the sum of the Van der Waals radii ( $r_{\text{vdw}}(\text{N})=1.54 \text{ \AA}$  and  $r_{\text{vdw}}(\text{I})=2.15 \text{ \AA}$ )

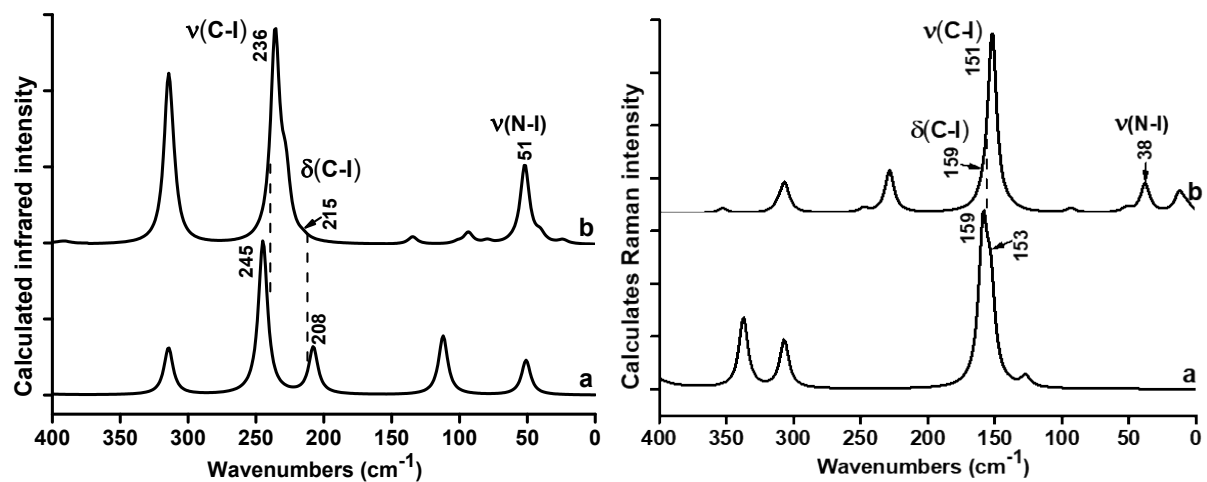
**Table S2:** Geometrical parameters calculated by DFT for TFBI-Piperazine, TFBI..(Piperazine)<sub>2</sub>, TFBI-diAzopyridine and TFBI..(Azopyridine)<sub>2</sub> complexes.

	Stretching C-I $\nu_{C-I}$		Bending C-I $\delta_{C-I}$		Stretching N-I (XB) $\nu_{N-I}$	
	Raman	IR (cm <sup>-1</sup> )	Raman	IR (cm <sup>-1</sup> )	Raman	IR
<b>Experimental</b>						
TFIB	156	243	142	209	-	-
<b>1</b>	144	229	160	213	61	67
<b>2</b>	149	231	159	210	74	69
<b>Calculated</b>						
TFBI					-	-
PBE0	159 (4)	245 (2)	153 (2)	208 (0.5)		
PBE0-GD3	158 (4)	244 (1)	153 (2)	208 (0.4)		
M06	157 (3)	243 (1)	151 (2)	204 (0.4)		
<b>1 TFBI..Piperazine</b>						
PBE0	151 (23)	237 (11)	156 (1.5)	212 (0.5)	70	70
PBE0-GD3	152 (21)	237 (12)	156 (3.4)	212 (0.5)	69	69
M06	153 (17)	237 (12)	157 (1.2)	209 (0.7)	73	71
<b>1 TFBI..(Piperazine)<sub>2</sub></b>						
PBE0	149 (56)	230 (38)	157 (1)	216 (0.7)	55	48
PBE0-GD3	150 (53)	229 (41)	159 (1)	217 (0.7)	62	62
M06	151 (39)	232 (35)	158 (1)	214 (0.9)	76	76
<b>2 TFBI..Azopyridine</b>						
PBE0	154 (8)	239 (10)	157 (2.5)	211 (0.4)	49	46
PBE0-GD3	154 (44)	239 (11)	158 (3)	211 (0.4)	46	46
M06	154 (36)	239 (11)	158 (2)	208 (0.5)	53	54
<b>2 TFBI..(Azopyridine)<sub>2</sub></b>						
PBE0	151 (124)	236 (30)	159 (3)	215 (0.4)	38	51
PBE0-GD3	152 (130)	235 (32)	160 (3)	215 (0.4)	52	56
M06	153 (104)	236 (33)	160 (3)	212 (0.5)	53	59

**Table S3:** Overview on the assignments of the TFIB, **1** and **2** vibrations in the spectral region from 300 to 50  $\text{cm}^{-1}$ . Comparison of the experimental vibrational frequencies (Raman and FIR) with computed frequencies (Intensities) for the fundamentals ( $\nu$ : stretching and  $\delta$ : deformation in  $\text{cm}^{-1}$ ). Intensities are given in brackets for the calculated values.



**Figure S3.** Calculated infrared (left) and Raman spectra (right) in the region 400 - 0 cm<sup>-1</sup> for a) TFBI b) 1 TFBI..(Piperazine)<sub>2</sub> compounds.



**Figure S4.** Calculated infrared (left) and Raman spectra (right) in the region 400 - 0 cm<sup>-1</sup> of a) TFBI b) 2 TFBI..(Azopyridine)<sub>2</sub> compounds.