

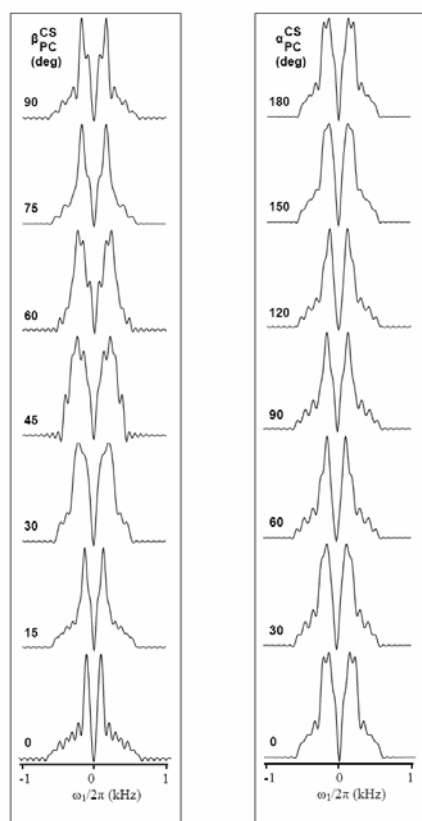
## Revealing molecular self-assembly and geometry of non-covalent halogen bonding by solid-state NMR spectroscopy

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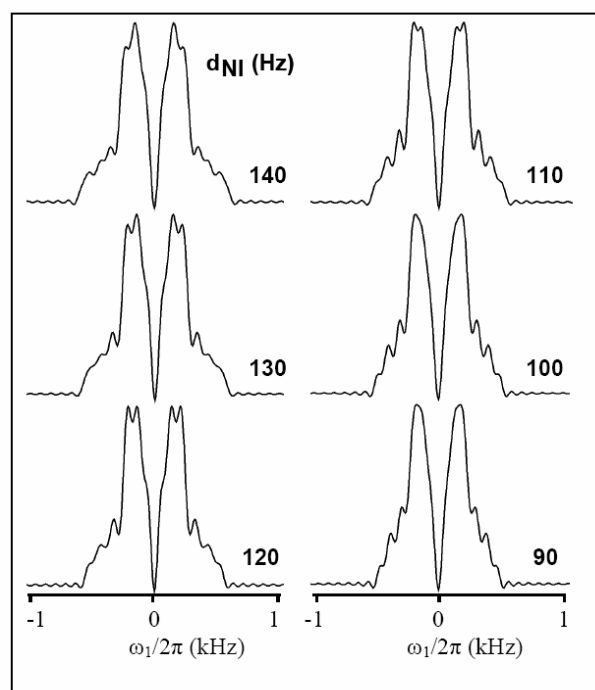
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### Supporting Information

#### A. Numerical simulations



**Figure S1.** Simulated <sup>15</sup>N solid-state NMR rotary resonance lineshapes for different values of the Euler angles  $\beta^{\text{CS}}$  and  $\alpha^{\text{CS}}$  that define the orientation of the <sup>15</sup>N chemical shift tensor relative to <sup>15</sup>N-<sup>127</sup>I axis. All calculations were done with the SIMPSON program and assume  $\omega_r/2\pi = \omega_{15\text{N}}/2\pi = 10$  kHz, the magnitude of chemical shift and dipolar tensors with  $\Delta\delta = -482$  Hz;  $\eta = 0.68$  and  $d_{\text{NI}} = 124$  Hz. (left) The dipolar tensor was aligned to the crystal frame. The  $\alpha$  and  $\gamma$  angles were equal to zero. (right) The  $\beta$  and  $\gamma$  was equal to  $23^\circ$  and  $0^\circ$ , respectively.



**Figure S2.** Simulated <sup>15</sup>N solid-state NMR rotary resonance lineshapes for different  $d_{\text{NI}}$  values of dipolar coupling. All calculations assume  $\omega_r/2\pi = \omega_{15\text{N}}/2\pi = 10$  kHz, the magnitude of chemical shift with  $\Delta\delta = -482$  Hz and  $\eta = 0.68$ . The  $\beta$  angle was equal to  $23^\circ$ , the  $\alpha$  and  $\gamma$  angles were equal to zero.

## B. Synthesis of $^{15}\text{N}$ labeled benzylamine

All reactions were carried out under argon in oven-dried glassware, using standard syringe and septum equipment. Solvent were analytical gradient purchased from ACROS and used without further purification. Separations were carried out by column chromatography (Fluka silica gel, 40-60  $\mu\text{m}$ ) unless otherwise indicated. Liquid-state  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advanced 250 instrument; chemical shifts are given in ppm relative to TMS and coupling constants in Hz. Potassium  $^{15}\text{N}$ -phthalimide (98%) was purchased from Euriso-Top and used as soon as received, all others reagents were purchased from Sigma-Aldrich or Acros and used as received without further purification unless otherwise indicated.

### $^{15}\text{N}$ -Benzylphthalimide

A 50 mL flask equipped with a stirring bar and a condenser was used. To a mixture of 1.0 g (5.3 mmol) of potassium  $^{15}\text{N}$ -phthalimide and 0.7g (5.0 mmol) of potassium carbonate, 5.5 mL (43.0 mmol) of benzyl chloride was added and heated to reflux for 3 h. The heating was then stopped and the solution was allowed to cool down at room temperature, the condenser was replaced by a short path distiller and the excess of benzyl chloride was distilled under vacuum (about 5 mmHg). The unreacted  $\text{K}_2\text{CO}_3$  was dissolved by 20 mL of a hydro-alcoholic solution (40/60). The resulting solid was filtered off, washed twice with 10 mL of diethyl ether and 1.2 g of the crude product (95% yield) were isolated. The product was used without further purification.  $^1\text{H}$  NMR : (250 MHz;  $\text{CDCl}_3$ ; TMS)  $\delta$  = 7.83 (dd,  $^3J(\text{H,H}) = 5.5$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 2H,  $\text{H}_{\text{arom}}$ ), 7.68 (dd,  $^3J(\text{H,H}) = 5.5$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 2H,  $\text{H}_{\text{arom}}$ ), 7.43 (m, 2H,  $\text{H}_{\text{arom}}$ ), 7.29 (m, 3H,  $\text{H}_{\text{arom}}$ ), 4.84 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR: (62.9 MHz;  $\text{CDCl}_3$ ; TMS)  $\delta$  = 168.1 (d,  $^1J(^{13}\text{C}, ^{15}\text{N}) = 12.9$  Hz,  $\text{C}=\text{O}$ ), 136.4, 134.0, 132.2 (d,  $^2J(^{13}\text{C}, ^{15}\text{N}) = 7.8$  Hz), 128.7, 128.6, 127.8, 123.4, 41.6 (d,  $^1J(^{13}\text{C}, ^{15}\text{N}) = 9.5$  Hz,  $^{15}\text{N}-\text{CH}_2\text{-Ph}$ ).

### $^{15}\text{N}$ -Benzylamine

In a 25 mL two necked flask fitted with a stirring bar and a condenser, 0.33 g (6.7 mmol) of hydrazine monohydrate was added to a solution of 1.2g (5.0 mmol) of  $^{15}\text{N}$ -benzylphthalimide in 10 mL of ethanol and heated under vigorous stirring for 2 h. The heating was then stopped and the solution was allowed to cool down to room temperature. 4.0 mL of concentrated hydrochloric solution (20 %) were added and the solution was heated for a further 5 min. The resulting white solid was filtered off. The filtrate was neutralized with 6 mL of concentrated sodium hydroxide solution (4.0 M). The resulting solution was extracted three times with 10 mL of diethyl ether. The organic layer was dried over anhydrous magnesium sulfate then the diethyl ether was evaporated. The product was obtained in 95% yield (0.5 g)

in form of light yellow oil. The product was used without further purification.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$ = 7.31, 7.29-7.25(m, 5H, benzyl), 3.81 (s, 2H,  $\text{CH}_2$ -Ph), 1.55 (s, 2H,  $^{15}\text{NH}_2$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$ = 143.3, 128.5, 127.1, 126.8, 46.5 (d,  $^1J(\text{C},^{15}\text{N})= 3.8$  Hz,  $^{15}\text{N-CH}_2$ ).

*$^{15}\text{N}$  labeled bis(4-iodobenzyl)-benzylamine (1)*

To a stirred solution of 0.24 g (2.2 mmol) of  $^{15}\text{N}$ -benzylamine and 0.50 g (2.2 mmol) of 4-iodobenzaldehyde in 10 mL of dichloromethane, 0.67g (3.2 mmol) of sodium triacetoxy borohydride was added and stirred for 12 hours at rt. The solution was quenched with 15 mL of a saturated aqueous solution of sodium bicarbonate. The aqueous phase was separated and then extracted three times with 10 mL of dichloromethane. The organic layer was washed with 10 mL of water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuum, 20 mL of a mixture petroleum ether/diethyl ether was added, a white solid precipitated, filtrated off and recrystallized from a mixture of dichloromethane/diethyl ether to afford the pure compound 1 (0.61 g; 52 % yield).  $R_f = 0.6$  (dichloromethane/petroleum ether 30:70).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$ = 7.63 (d,  $^3J(\text{H},\text{H})= 8$  Hz, 4H, Ph-I), 7.40-7.20 (m, 7.33-7.31-7.28-7.25, 5H,  $\text{H}_{\text{arom}}$ ), 7.12 (d,  $^3J(\text{H},\text{H})= 8$  Hz, 4H, Ph-I), 3.51 (s, 2H,  $\text{CH}_2$ -Ph), 3.46 (s, 4H,  $\text{CH}_2$ -PhI).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$ = 138.1 (d,  $^2J(\text{C},^{15}\text{N})= 1.3$  Hz, Ph-I), 137.9, 136.4, 129.7, 127.7, 127.3, 126.1, 91.2, 56.9 (d,  $^1J(\text{C},^{15}\text{N}) = 4.5$  Hz,  $\text{CH}_2$ -Ph), 56.3 (d,  $^1J(\text{C},^{15}\text{N})= 4.4$  Hz,  $\text{CH}_2$ -Ph-I). HRMS (DEI+) m/z calcd. for  $\text{C}_{21}\text{H}_{19}\text{N}_{15}\text{I}_2$ : 539.9577; found: 539.9697.