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# Quantitative analysis of weak non-covalent interactions in (*Z*)-3-(4-halophenyl)-2-(pyridin-2/3/4-yl) acrylonitriles

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**General Methods:**

The $^{1}H$, $^{13}C$ NMR spectra were recorded on a Bruker 500 instrument. Chemical shifts (δ) are reported in ppm relative to residual solvent signals for $^{1}H$ and $^{13}C$ NMR ($^{1}H$ NMR: 7.26 ppm for CDCl3 and 13C NMR: 77.0 ppm for CDCl3). Multiplicities are reported as follows: s, singlet, d, doublet, dd, doublets of doublets, t, triplet, q, quartet, m, multiplet, c, complex, and br, broad.

**Absorbance (UV–vis) spectra**

Absorbance spectra were measured using a Cary 300 (Agilent) spectrometer equipped with a deuterium and halogen lamp. For measurements (190–700 nm) in solution, the solvents(chloroform) used were of spectroscopic grade and were subjected to preliminary checks to ensure the absence of absorbing impurities within the scanned spectral ranges. For powder samples, the absorption spectra were measured with KBr pellets using a DT 1000 CE light source (Analytical Instrument Systems, Inc.).

**Experimental procedure**

**General experimental procedure for synthesis of (Z)-3-(4-halogenatedphenyl)-2-(pyridineyl) acrylonitrile derivatives**

The (Z)-3-(4-halogenatedphenyl)-2-(pyridinyl) acrylonitrile derivatives was prepared as reported earlier. A mixture of pyridylacetonitrile (1.1 mmol, 1.1 equv.) and appropriate benzaldehyde (1.0 mmol, 1 equv.) was heated at 140 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature and an oily residue was obtained. The products were obtained as precipitates when the oily residue stirred with 20 mL of 2 M NaOH solution for 12h at room temperature. The precipitates were washed with water and filtered out. The final product was dried under the vacuum and the compounds were purified by recrystallization from either hexane: chloroform (1:1, v/v) or cyclohexane: chloroform (1:1, v/v) mixture. The synthesized compounds were characterized by spectroscopy methods (IR, $^{1}H$, $^{13}C$ NMR) and single x-ray diffraction studies.

**1. Synthesis of (Z)-3-(4-flourophenyl)-2-(pyridine-2-yl) acrylonitrile (2F)**

The **2F** synthesized by using the reported procedure[1]. The compounds characterization details: yield 30 % and m.p 91-92 ° C; IR (KBr, $cm^{-1}$) 3048, 3049, 2215, 1658, 1592, 1507, 1234 and 777. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.65 (m, 1H), 8.46 (s,1H), 8.02(d, 2H), 7.80(d, 2H), 7.31 (m, 1H) and 7.19(d, 2H). The NMR spectral are consistent with literature repots[1].

**2. Synthesis of (Z)-3-(4-chlorophenyl)-2-(pyridine-2-yl) acrylonitrile (2Cl)**

The **2Cl** synthesized by using the reported procedure[1]. The compounds characterization details: yield 40 % and m.p 70 -71 ° C; IR (KBr, $cm^{-1}$) 3098, 3071, 3048, 2217, 1645, 1584, 1492, 822 and 778. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.67 (dd, 1H), 8.54 (s,1H), 7.96 (d, 2H), 7.82(m, 2H), 7.47 (d, 2H) and 7.34(m, 1H). The NMR spectral are consistent with literature repots[1].

**3. Synthesis of (Z)-3-(4-bromophenyl)-2-(pyridine-2-yl) acrylonitrile (2Br)**

The **2Br** synthesized by using the reported procedure. The compounds characterization details: yield 40 % and m.p 132 -134 ° C; IR (KBr, $cm^{-1}$) 3081, 3053, 3002, 2219, 1604, 1583, 1489, 1467, 1430, 1352, 814 and 777. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.68-8.66 (m, 1H), 8.54 (s,1H), 7.89-7.88 (dd, 2H), 7.84-7.82(dd, 2H), 7.65 (dd, 2H) and 7.35-7.32(m, 1H).

**4. Synthesis of (Z)-3-phenyl-2-(pyridine-2-yl) acrylonitrile (2H)**

The **2H** synthesized by using the reported procedure[2]. The compounds characterization details: yield 70 % and m.p 62 -63 ° C; IR (KBr, $cm^{-1}$) 3081, 3054, 3006, 2215, 1676, 1579, 1567, and 779. $^1H$ NMR(300 MHz, CDCl3, δ in ppm ) 8.64 (d, 1H), 8.47 (s,1H), 8.00 (m, 2H), 7.81(m, 2H), 7.49 (m, 3H) and 7.30(m, 1H). The NMR spectral are consistent with literature repots[2].

**5. Synthesis of (Z)-3-(4-flourophenyl)-2-(pyridine-3-yl) acrylonitrile (3F)**

The **3F** synthesized by using the reported procedure[1]. The compounds characterization details: yield 30 % and m.p 112 -114 ° C; IR (KBr, $cm^{-1}$) 3043, 2214, 1668, 1599, 1510, 1230 and 774. $^1H$ NMR(500

MHz, CDCl3, δ in ppm ) 8.98 (s,1H), 8.67 (d, 1H), 8.04 (d, 1H), 7.95(d, 2H), 7.60(s, 1H), 7.47 (m, 1H) and 7.21 (d, 2H). The NMR spectral are consistent with literature repots[1].

**6. Synthesis of (Z)-3-(4-chlorophenyl)-2-(pyridine-3-yl) acrylonitrile (3Cl)**

The **3Cl** synthesized by using the reported procedure[1]. The compounds characterization details: yield 25 % and m.p 109 -110 ° C; IR (KBr, $cm^{-1}$) 3080, 3051, 2214, 1651, 1588, 1493, 821 and 774. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.99 (s,1H), 8.67 (d, 1H), 8.05 (d, 1H), 7.87(d, 2H), 7.60(s, 1H), 7.50 (m, 1H) and 7.48 (d, 2H). The NMR spectral are consistent with literature repots[1].

**7. Synthesis of (Z)-3-(4-bromophenyl)-2-(pyridine-3-yl) acrylonitrile (3Br)**

The **3Br** synthesized by using the reported procedure. The compounds characterization details: yield 40 % and m.p 114 -116 ° C; IR (KBr, $cm^{-1}$) 3051, 2948, 2216, 1604, 1584, 1491, 1430, 1406, 1360, 815 and 704. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.96-8.95 (d, 1H), 8.69-8.67 (dd,1H), 8.01-7.99 (dd, 1H), 7.82(d, 2H), 7.65 (d, 2H), 7.54(s, 1H) and 7.45-7.43 (m,1H).

$H^1$

**8. Synthesis of (Z)-3-phenyl-2-(pyridine-3-yl) acrylonitrile (3H)**

The **3H** synthesized by using the reported procedure[2]. The compounds characterization details: yield 25 % and m.p 100 -101 ° C; IR (KBr, $cm^{-1}$) 3097, 3046, 2212, 1660, 1572 and 754. $^1H$ NMR(300 MHz, CDCl3, δ in ppm ) 8.91 (d,1H), 8.62 (dd, 1H), 7.96 (m, 2H), 7.55 (s, 5H), and 7.01(m, 1H). The NMR spectral are consistent with literature repots[2].

**9. Synthesis of (Z)-3-(4-flourophenyl)-2-(pyridine-4-yl) acrylonitrile (4F)**

The **4F** synthesized by using the reported procedure[1]. The compounds characterization details: yield 60 % and m.p 151-152 ° C; IR (KBr, $cm^{-1}$) 3056, 2927, 2214, 1674, 1594, 1515, 1419, 1249 and 771. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.72 (d,2H), 7.98 (d, 2H), 7.70(s, 1H), 7.60(d, 2H) and 7.22 (d, 2H). The NMR spectral are consistent with literature repots[1, 3].

**10. Synthesis of (Z)-3-(4-chlorophenyl)-2-(pyridine-4-yl) acrylonitrile (4Cl)**

The **4Cl** synthesized by using the reported procedure. The compounds characterization details: yield 35 % and m.p 97 -98 ° C; IR (KBr, $cm^{-1}$) 3053, 3025, 2213, 1675, 1588, 1550, 1495, 819 and 775. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.66 (d,2H), 7.83 (d, 2H), 7.62 (s, 1H), 7.53 (d, 2H) and 7.43 (d, 2H). The NMR spectral are consistent with literature repots[1, 3].

**11. Synthesis of (Z)-3-(4-bromophenyl)-2-(pyridine-4-yl) acrylonitrile (4Br)**

The **4Br** synthesized by using the reported procedure[2]. The compounds characterization details: yield 45 % and m.p 114 -116 ° C; IR (KBr, $cm^{-1}$) 3057, 3026, 2214, 1664, 1575 and 761. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.73 (d,2H), 7.83 (d, 2H), 7.70 (m, 3H) and 7.62 (d, 2H). The NMR spectral are consistent with literature repots[3].

**12. Synthesis of (Z)-3-phenyl-2-(pyridine-3-yl) acrylonitrile (4H)**

The **4H** synthesized by using the reported procedure[2]. The compounds characterization details: yield 25 % and m.p 100 -101 ° C; IR (KBr, $cm^{-1}$) 3097, 3046, 2212, 1660, 1572 and 754. $^1H$ NMR(500 MHz, CDCl3, δ in ppm ) 8.73 (d,2H), 7.98 (m, 2H), 7.76 (s, 1H), 7.61 (d, 2H), and 7.54(m, 3H). The NMR spectral are consistent with literature repots[3].

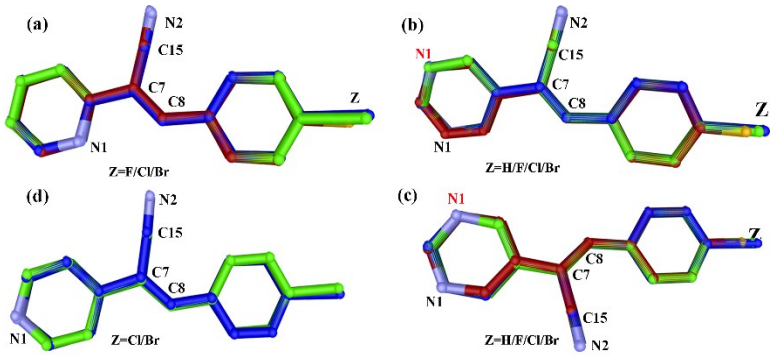


**Fig. S1** Structural superimposition diagrams of (a) **2py;** (b and c) two different views of **3py** and (d) **4py** family. The *anti* conformation of pyridine ring in **3F** is shown. Color codes: carbon atoms in 2F, 3F and 4F in red; **2Cl**, **3Cl** and **4Cl** in green; **2Br**, **3Br** and **4Br** in blue and **3H** in purple.

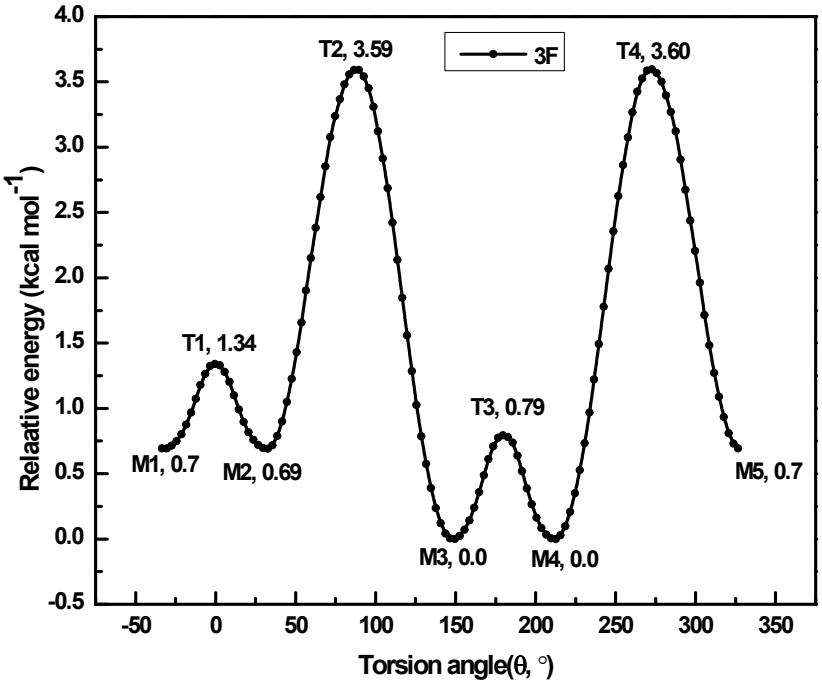


**Fig. S2** The potential energy surface for the torsion angle C2-C1-C7-C8 in **3F**. The relative energies of various conformers are indicated and **M1** is the crystal structure conformer.

**Table S1** The torsion angle (C2-C1-C7-C8) of different conformers and relative energies of various conformers.

| Conformation | 3F | |
|---|---|---|
| | Torsion angle (°) | Relative energy (kcal mol$^{-1}$) |
| **M1** | -33.35 | 0.70 |
| **T1** | -0.35 | 1.34 |
| **M2** | 32.65 | 0.69 |
| **T2** | 86.65 | 3.59 |
| **M3** | 146.65 | 0.0 |
| **T3** | 179.65 | 0.79 |
| **M4** | 212.65 | 0.0 |
| **T4** | 272.65 | 3.60 |
| **M5** | 326.65 | 0.70 |

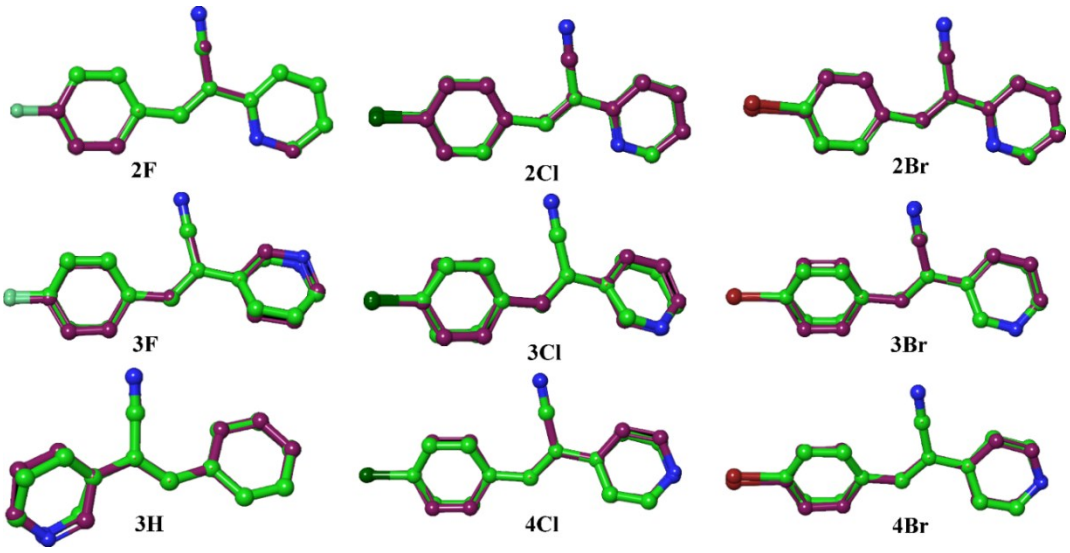


**Fig. S3** The overlay diagrams between crystal structures (purple) and the respective optimized structures (green) in gas phase.

**Table S2** The selected torsion angles that describe the molecular conformation.

| Compound | Torsion angles (°) | | | | | |
|---|---|---|---|---|---|---|
| | C2(N1)*/C1/C7/C8 | | C1/C7/C8/C9 | | C7/C8/C9/C10 | |
| | XRD | DFT | XRD | DFT | XRD | DFT |
| **2F*** | -3.6 | 0.0 | 179.0 | 180.0 | -174.4 | 180.0 |
| **2Cl*** | -8.3 | 0.0 | -175.2 | 180.0 | -178.6 | 180.0 |
| **2Br*** | -2.0 | 0.0 | -179.6 | 180.0 | -172.4 | 180.0 |
| **3H** | -8.3 | -33.7 | -179.6 | 178.4 | 162.2 | 160.9 |
| **3F** | 169.0 | 146.5 | 179.6 | 178.5 | -175.1 | 161.8 |
| **3Cl** | -15.1 | -33.6 | -173.4 | 178.4 | -176.6 | 161.6 |
| **3Br** | -14.7 | -31.9 | -178.9 | 177.7 | -174.3 | 163.5 |
| **4Cl** | -5.7 | -29.4 | -177.0 | 179.4 | -175.4 | 163.0 |
| **4Br** | -6.4 | -26.2 | 178.6 | 177.7 | 174.9 | 163.5 |

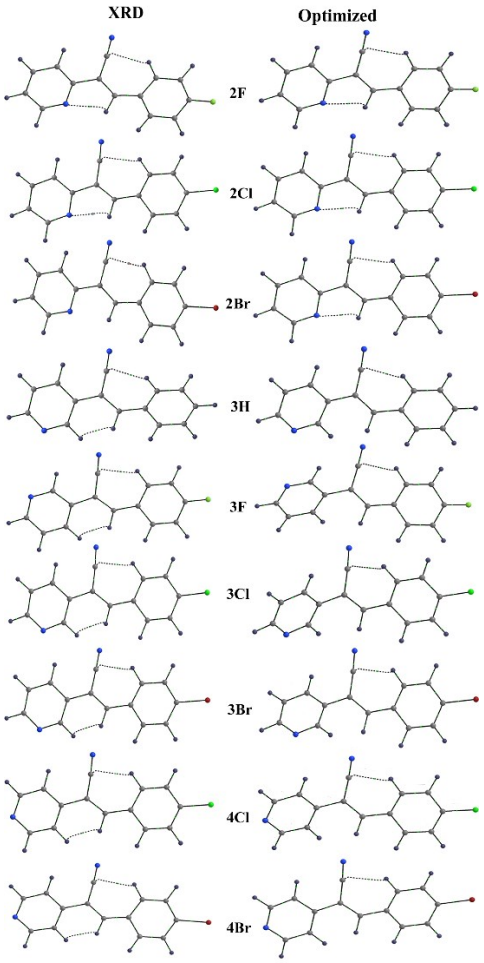


**Fig. S4** The Molecular graphs showing the bond critical points (BCP's) in XRD and optimized structures.

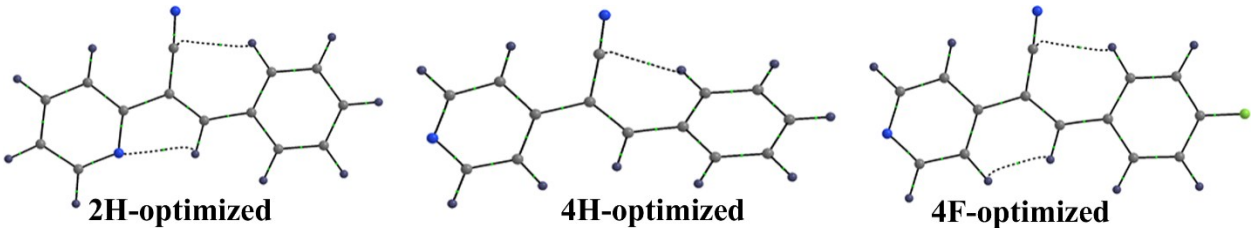


**Fig. S5** The Molecular graphs showing BCP's in the optimized structures.

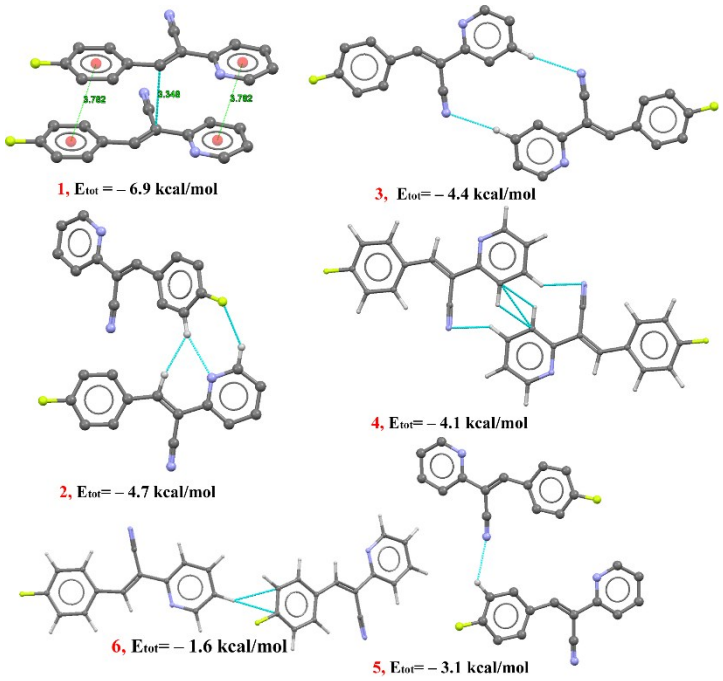


**Fig. S6** The selected molecular dimers in **2F** showing intermolecular contacts along with their interaction energies ($E_{tot}$)

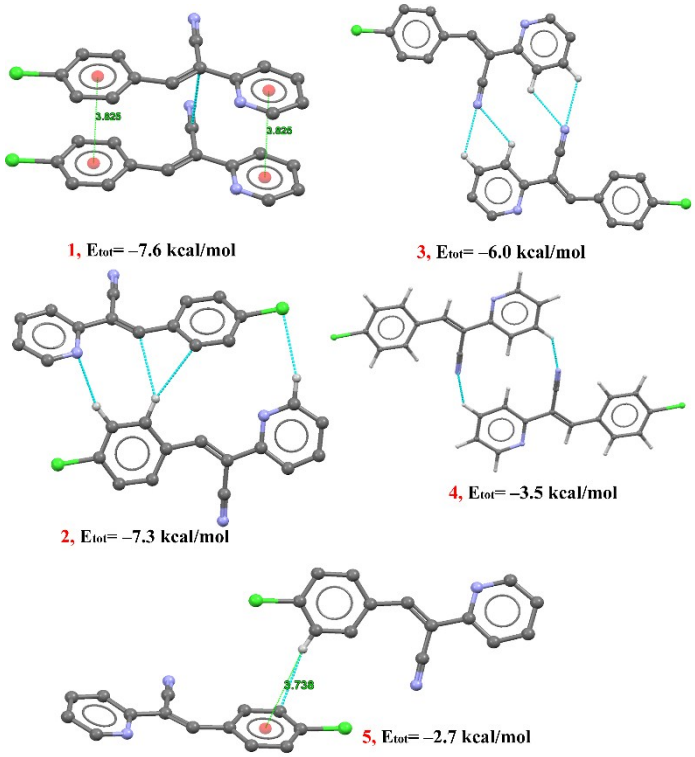


**Fig. S7** The selected molecular dimers in **2Cl** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

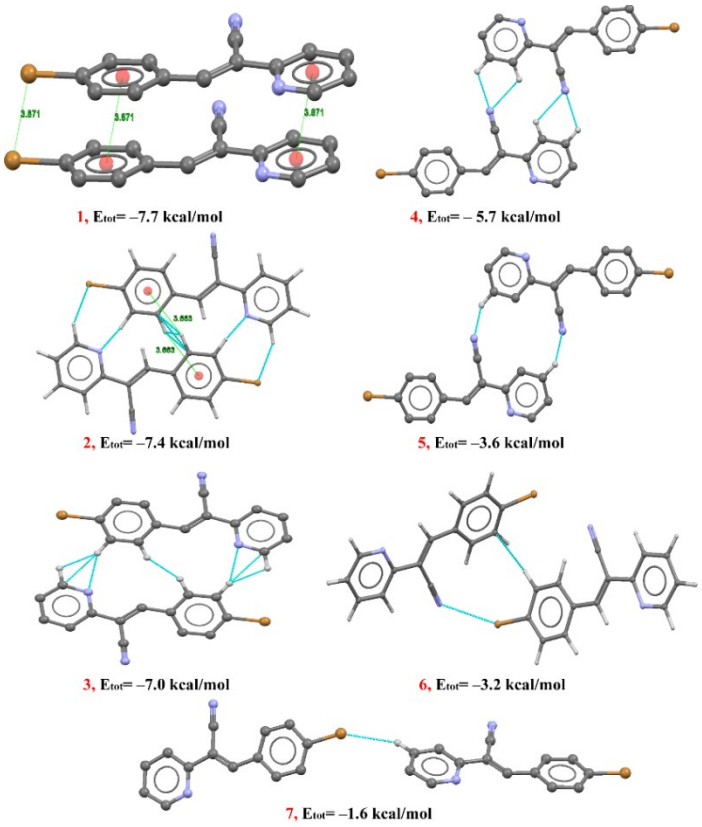


**Fig. S8** The selected molecular dimers in **2Br** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

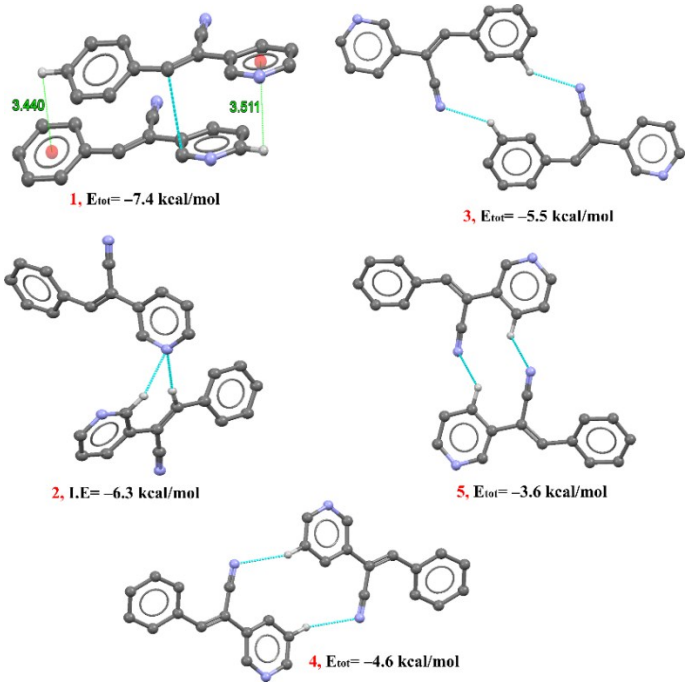


**Fig. S9** The selected molecular dimer in **3H** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

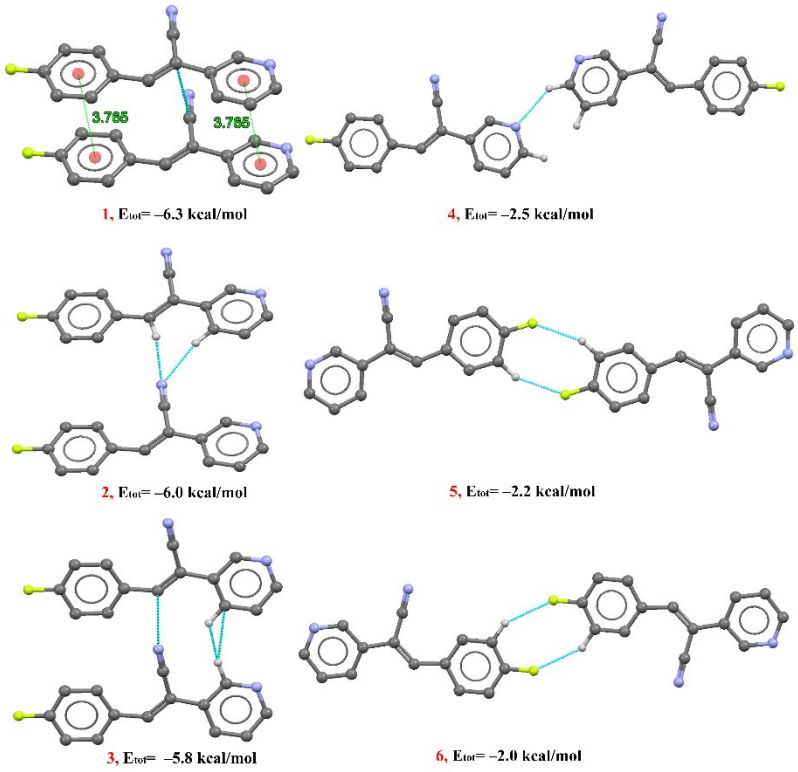


**Fig. S10** The selected molecular dimers in **3F** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

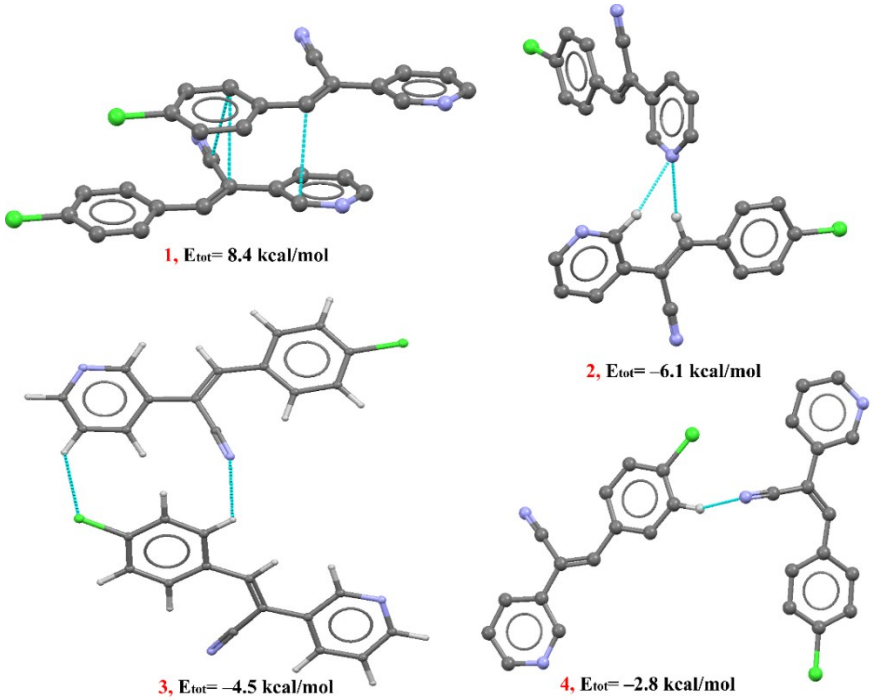


**Fig. S11** The selected molecular dimers in **3Cl** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

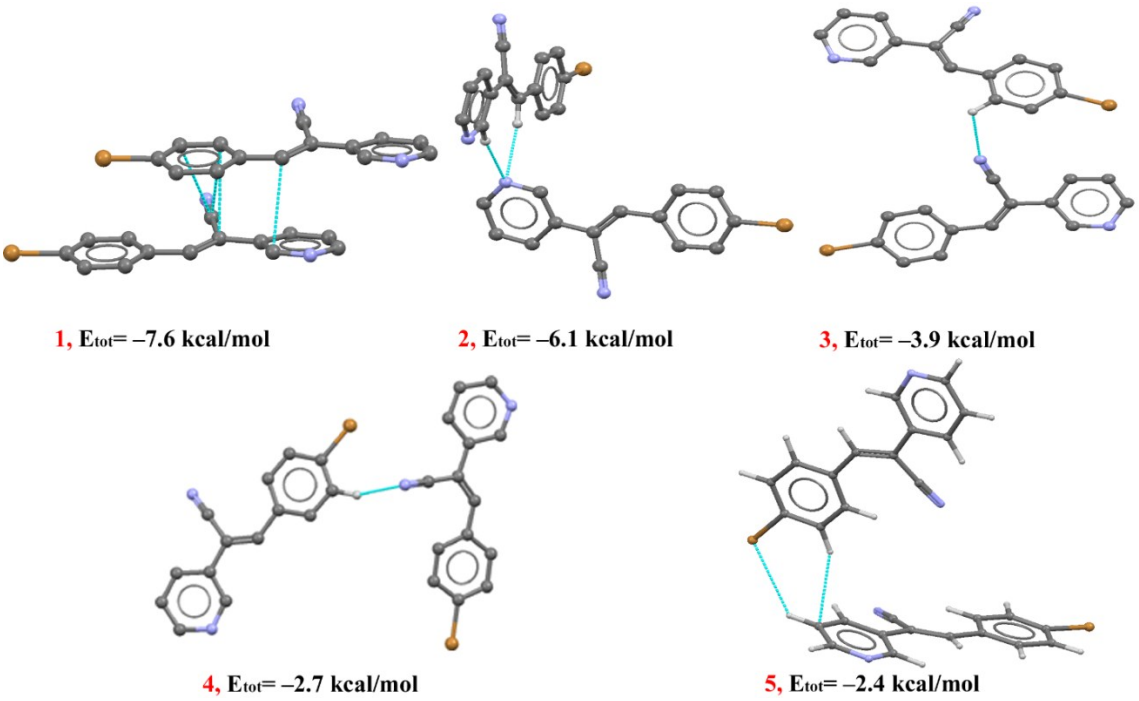


**Fig. S12** The selected molecular dimers in **3Br** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

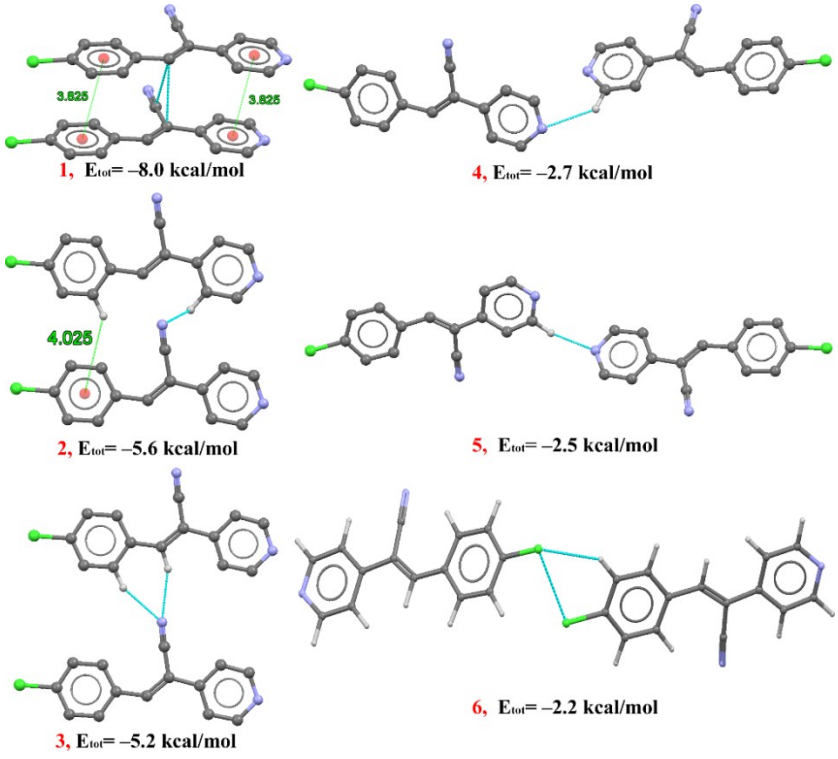


**Fig. S13** The selected molecular dimers in **4Cl** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

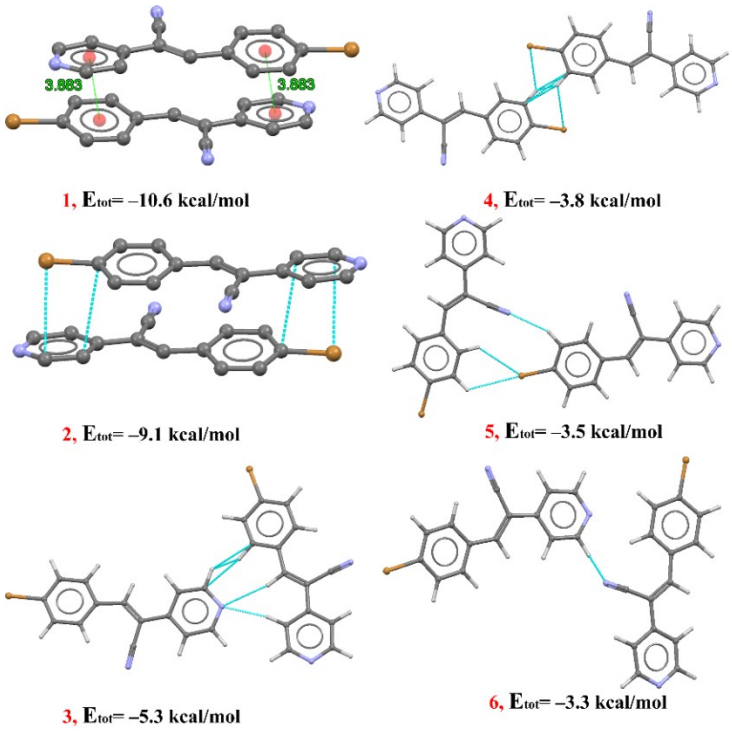


**Fig. S14** The selected molecular dimers in **4Br** showing intermolecular contacts along with their interaction energies ($E_{tot}$).

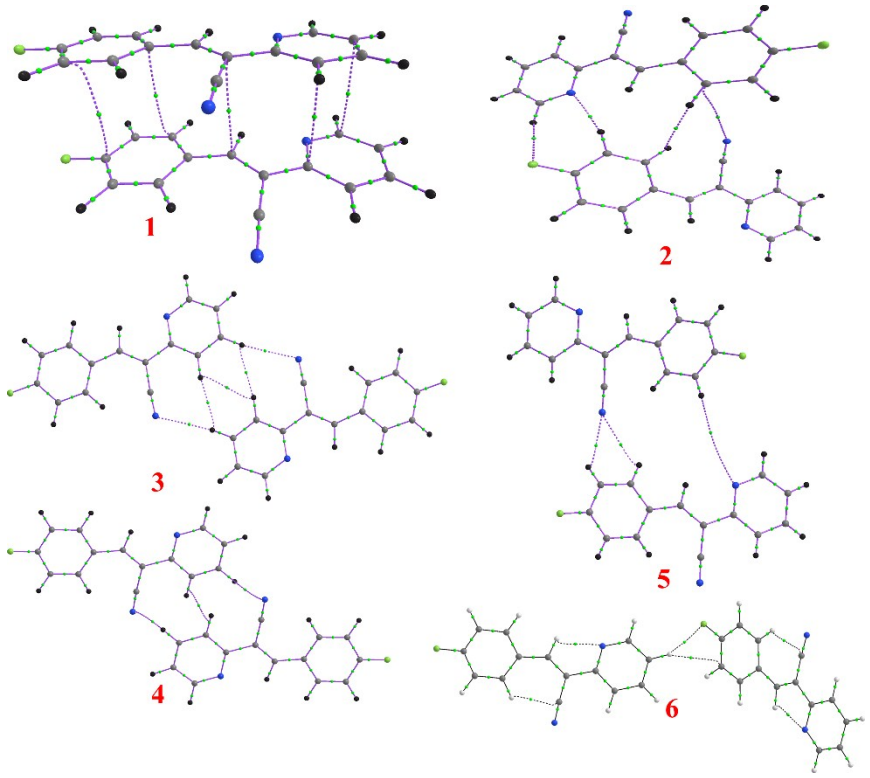


**Fig. S15** Molecular graphs showing BCP's in the selected molecular dimers in **2F.**

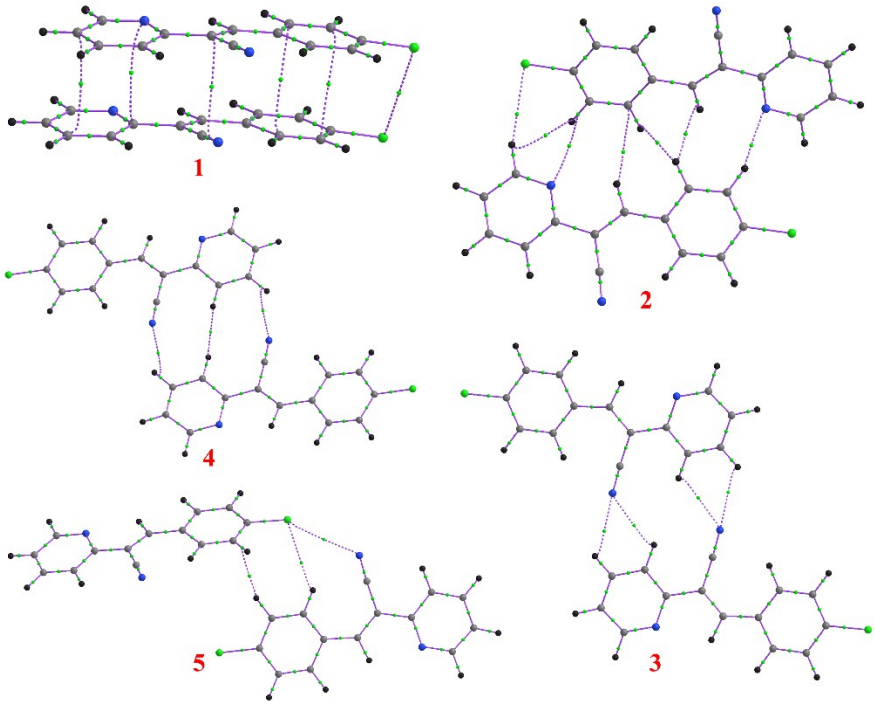


**Fig. S16** Molecular graphs showing BCP's in the selected molecular dimers in **2Cl.**

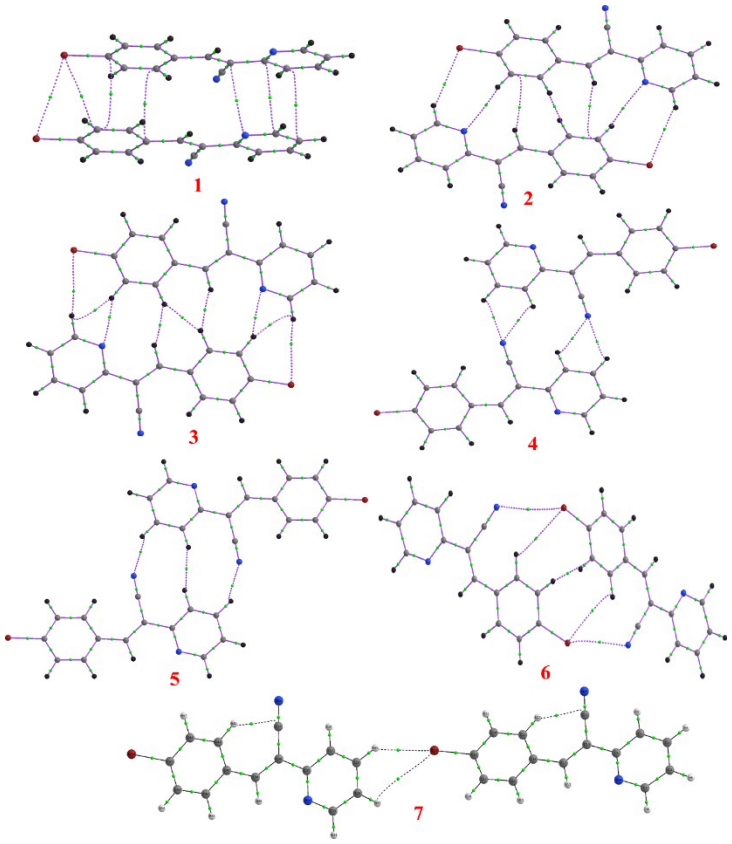


**Fig. S17** Molecular graphs showing BCP's in the selected molecular dimers in **2Br.**

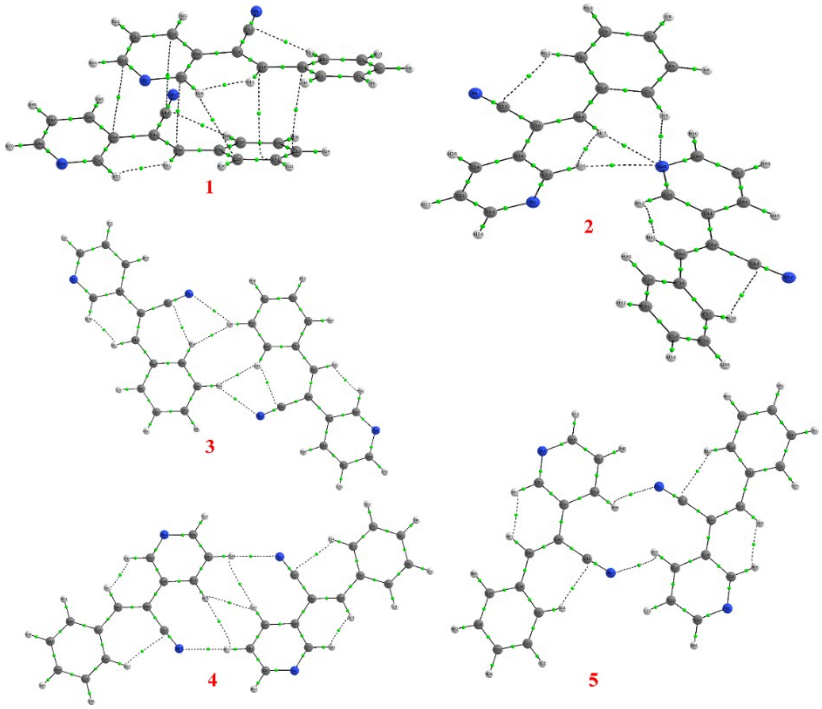


**Fig. S18** Molecular graphs showing BCP's in the selected molecular dimers in **3H.**

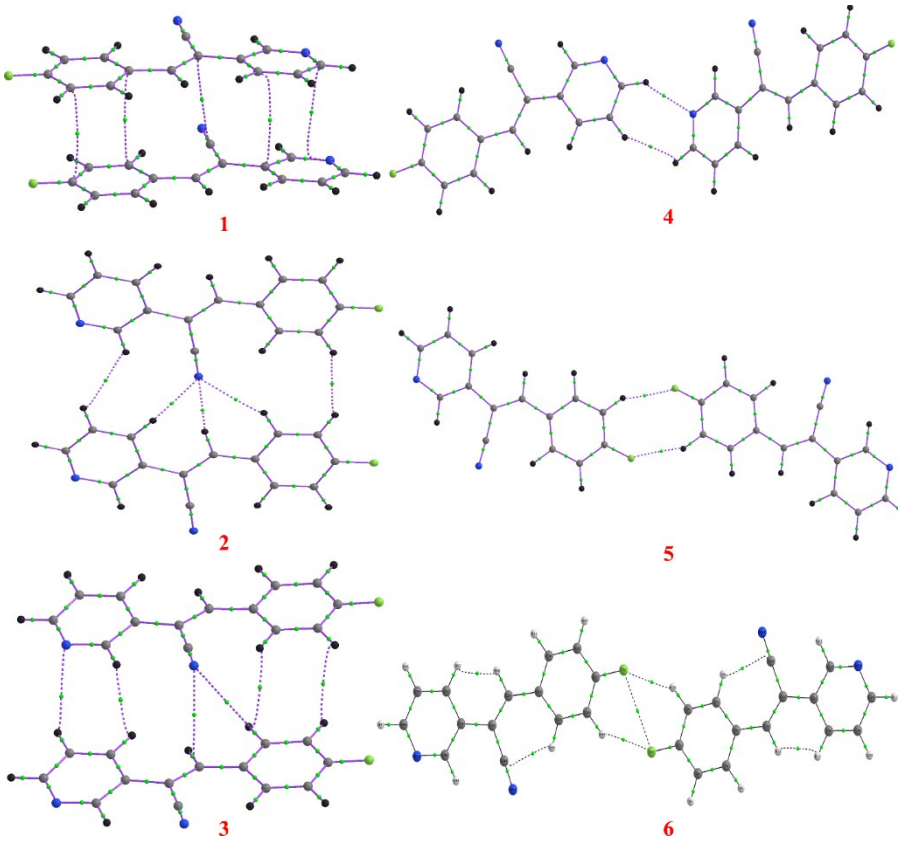


**Fig. S19** Molecular graphs showing BCP's in the selected molecular dimers in **3F.**

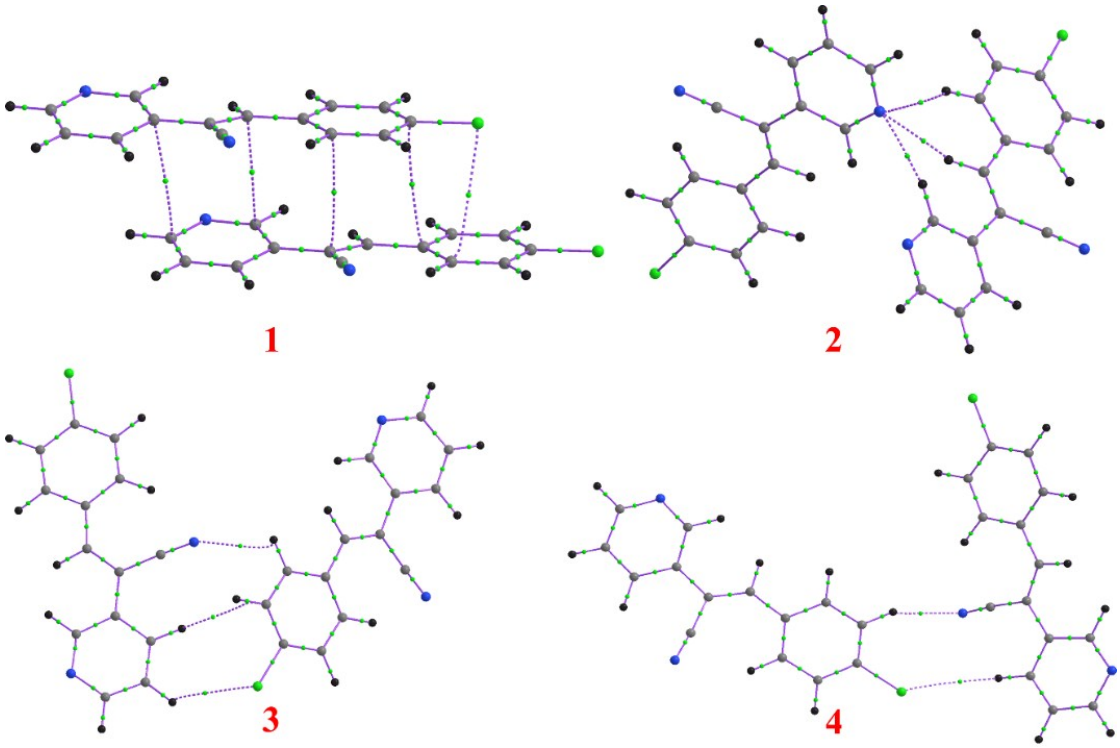


**Fig. S20** Molecular graphs showing BCP's in the selected molecular dimers in **3Cl.**

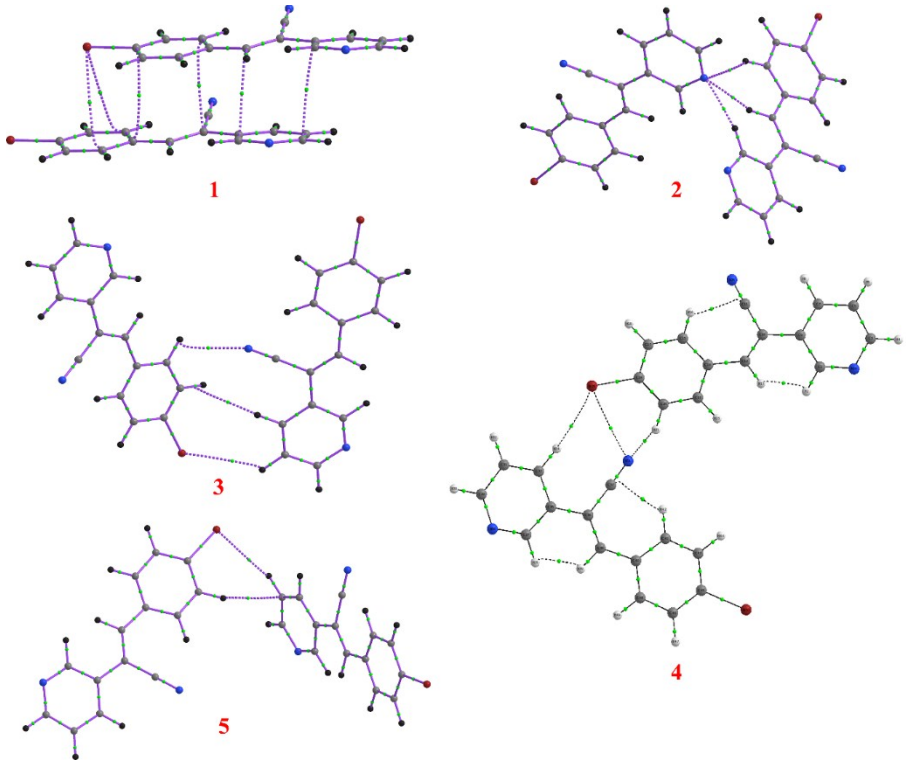


**Fig. S21** Molecular graphs showing BCP's in the selected molecular dimers in **3Br.**

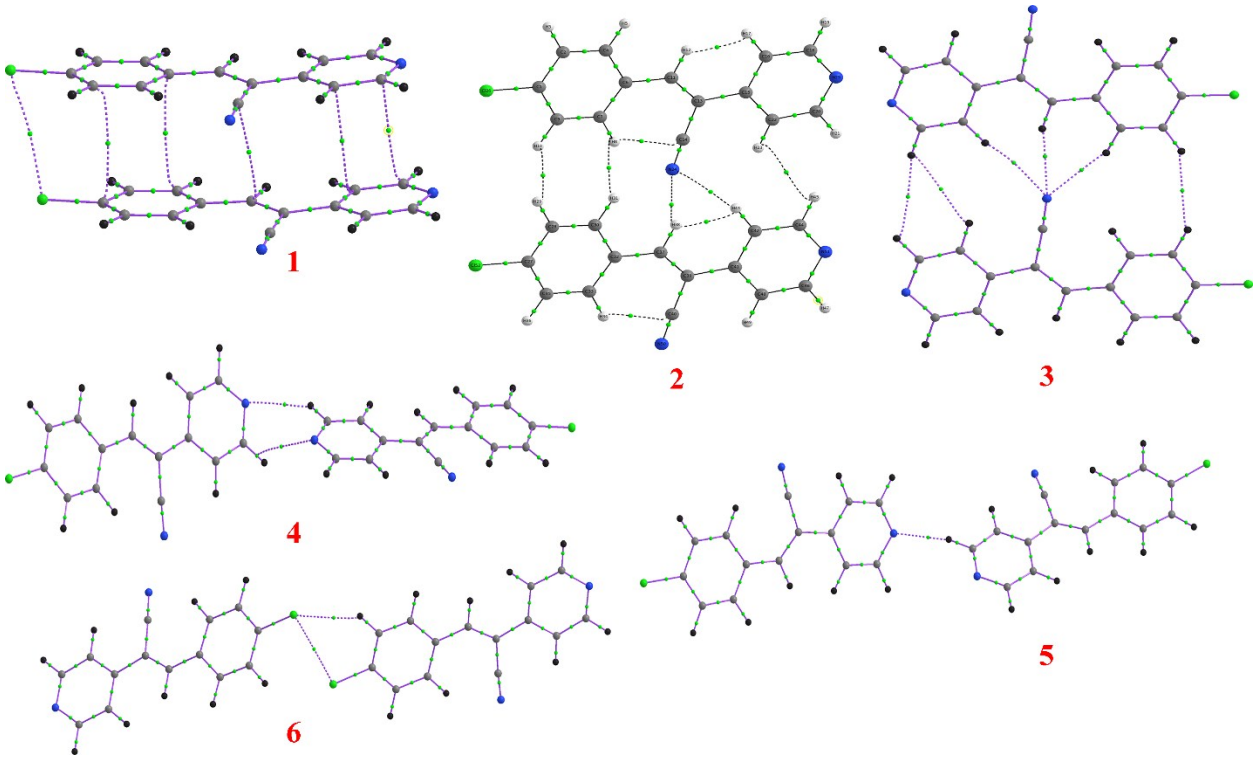


**Fig. S22** Molecular graphs showing BCP's in the selected molecular dimers in **4Cl.**

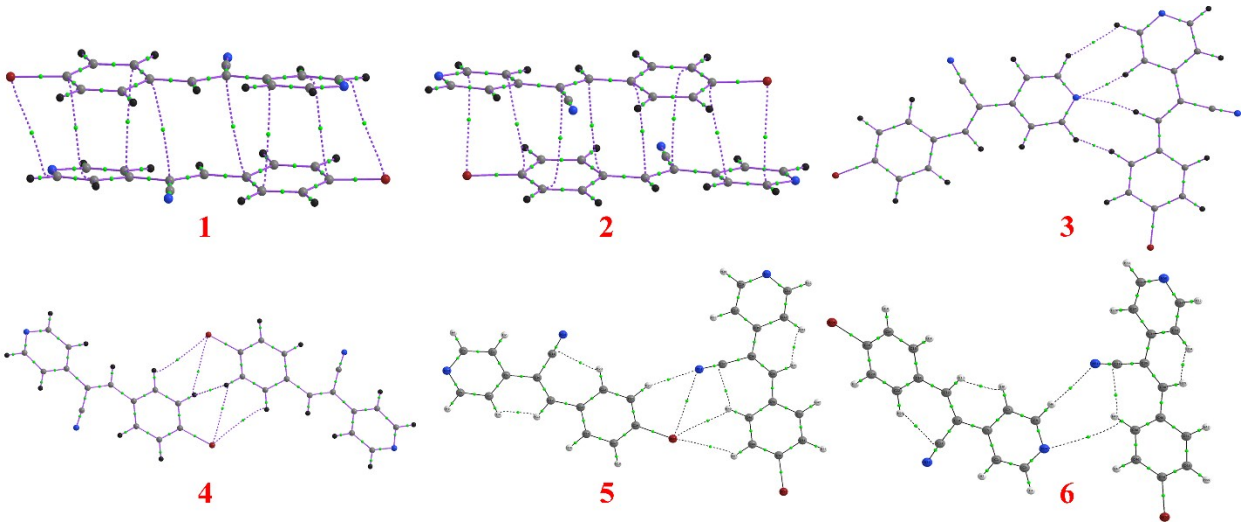


**Fig. S23** Molecular graphs showing BCP's in the selected molecular dimers in **4Br.**

**Table S3** Topological parameters for selected molecular pairs in **2F**.

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C8···C7 | 3.35 | –6.9/–5.86 | 3.357 | 0.0060 | 0.0176 | –0.00297 | 0.00368 | 0.93 |
| | C10···C9 (π···π) | 4.20 | | 3.538 | 0.0056 | 0.0149 | –0.00262 | 0.00317 | 0.82 |
| | C1···C6 (π···π) | 3.43 | | 3.461 | 0.0054 | 0.0151 | –0.00256 | 0.00317 | 0.81 |
| | C12···C13 (π···π) | 3.46 | | 3.762 | 0.0054 | 0.0142 | –0.00242 | 0.00299 | 0.76 |
| | C3···C4 (π···π) | 3.44 | | 3.623 | 0.0055 | 0.0147 | –0.00241 | 0.00304 | 0.76 |
| | | | | | | | | | |
| 2 | N1···H13–C13 | 2.44, 156.5 | –4.7/ –2.58 | 2.456 | 0.0119 | 0.0345 | –0.00643 | 0.00753 | 2.01 |
| | C3–H3···F1 | 2.64, 142.3 | | 2.662 | 0.0054 | 0.0210 | –0.00376 | 0.00451 | 1.18 |
| | | | | | | | | | |
| 3 | C5–H5···N2 | 2.80, 163.8 | –4.4/–3.61 | 2.826 | 0.0047 | 0.0142 | –0.00250 | 0.00302 | 0.79 |
| | N2···H5–C5 | 2.80, 163.8 | | 2.826 | 0.0047 | 0.0142 | –0.00250 | 0.00302 | 0.79 |
| | | | | | | | | | |
| 4 | C5–H5···N2 | 3.07, 110.7 | –4.1/–3.01 | 3.192 | 0.0039 | 0.0126 | –0.00196 | 0.00256 | 0.62 |
| | N2···H5–C5 | 3.07, 110.7 | | 3.192 | 0.0039 | 0.0126 | –0.00196 | 0.00256 | 0.62 |
| | | | | | | | | | |
| 5 | C11–H11···N2 | 2.57, 126.0 | –3.1/–2.61 | 2.692 | 0.0073 | 0.0262 | –0.00410 | 0.00533 | 1.29 |
| | C10–H10···N2 | 2.78, 118.6 | | 2.919 | 0.0052 | 0.0190 | –0.00297 | 0.00386 | 0.94 |
| | | | | | | | | | |
| 6 | C4–H4···F1 | 2.67, 132.5. | -1.6 / -0.48 | 2.697 | 0.0055 | 0.0228 | -0.00400 | 0.00485 | 1.26 |
| | C4–H4···C11 | 2.81,143 | | 2.877 | 0.0062 | 0.0194 | -0.00316 | 0.00040 | 0.99 |

**Table S4** Topological parameters for selected molecular pairs in **2Cl.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | N2···C7 | 3.34 | –7.6/–5.87 | 3.975 | 0.0067 | 0.0199 | –0.00328 | 0.00413 | 1.03 |
| | C13···C11 (π···π) | 3.51 | | 3.633 | 0.0055 | 0.0147 | –0.00256 | 0.00311 | 0.81 |
| | C14···C10 (π···π) | 3.52 | | 3.614 | 0.0055 | 0.0143 | –0.00253 | 0.00305 | 0.80 |
| | C5···C4 (π···π) | 3.47 | | 3.629 | 0.0054 | 0.0137 | –0.00237 | 0.00290 | 0.75 |
| | C1···N1 (π···π) | 3.48 | | 3.580 | 0.0046 | 0.0130 | –0.00228 | 0.00277 | 0.72 |
| | Cl1···Cl1 | 3.83 | | 3.827 | 0.0041 | 0.0135 | –0.00166 | 0.00252 | 0.52 |
| | | | | | | | | | |
| 2 | N1···H11–C11 | 2.53, 160.9 | –7.3/–3.45 | 2.557 | 0.0093 | 0.0266 | –0.00499 | 0.00582 | 1.57 |
| | C8–H8···H10–C10 | 2.43 | | 2.731 | 0.0058 | 0.0196 | –0.00321 | 0.00406 | 1.01 |
| | C10–H10···H10–C10 | 2.44 | | 2.712 | 0.0055 | 0.0177 | –0.00296 | 0.00370 | 0.93 |
| | Cl1···H3–C3 | 2.93, 160.9 | | 2.944 | 0.0059 | 0.0184 | –0.00286 | 0.00373 | 0.90 |
| | C11–H11···N1 | 2.53, 160.9 | | 3.605 | 0.0037 | 0.0122 | –0.00190 | 0.00248 | 0.60 |
| | | | | | | | | | |
| 3 | C5–H5···N2 | 2.74, 120.0 | –6.0/–5.11 | 2.788 | 0.0067 | 0.0220 | –0.00376 | 0.00463 | 1.19 |
| | N2···H5–C5 | 2.74,120.0 | | 2.788 | 0.0067 | 0.0220 | –0.00376 | 0.00463 | 1.19 |
| | C6–H6···N2 | 2.73, 120.3 | | 2.797 | 0.0063 | 0.0211 | –0.00355 | 0.00441 | 1.12 |
| | N2···H6–C6 | 2.73, 120.3 | | 2.797 | 0.0063 | 0.0211 | –0.00355 | 0.00441 | 1.12 |
| | | | | | | | | | |
| 4 | C5–H5···N2 | 2.90 104.1 | –3.5/–2.11 | 3.218 | 0.0055 | 0.0190 | –0.00289 | 0.00382 | 0.91 |
| | N2···H5–C5 | 2.90, 104.1 | | 3.218 | 0.0055 | 0.0190 | –0.00289 | 0.00382 | 0.91 |
| | | | | | | | | | |
| 5 | C13···H13–C13 (C–H ···π) | 2.80, 145.3 | –2.7/–0.95 | 3.002 | 0.0077 | 0.0246 | –0.00397 | 0.00506 | 1.25 |

**Table S5** Topological parameters for selected molecular pairs in **2Br.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C9···C14 (π···π) | 3.41 | –7.7/–6.00 | 3.619 | 0.0061 | 0.0163 | –0.00279 | 0.00344 | 0.88 |
| | C11···C12 (π···π) | 3.44 | | 3.750 | 0.0059 | 0.0159 | –0.00273 | 0.00335 | 0.86 |
| | Br1···Br1 | 3.87 | | 3.873 | 0.0058 | 0.0185 | –0.00266 | 0.00364 | 0.84 |
| | C11···Br1 | 3.73 | | 3.851 | 0.0050 | 0.0153 | –0.00235 | 0.00309 | 0.74 |
| | C1···C6 (π···π) | 4.08 | | 3.770 | 0.0050 | 0.0126 | –0.00220 | 0.00267 | 0.69 |
| | N1···C6 (π···π) | 4.08 | | 3.621 | 0.0042 | 0.0119 | –0.00214 | 0.00256 | 0.67 |
| | C3···C1 (π···π) | 3.57 | | 3.587 | 0.0043 | 0.0126 | –0.00209 | 0.00262 | 0.66 |
| | | | | | | | | | |
| 2 | C10–H10···H10–C10 | 2.66 | –7.4/–4.32 | 3.240 | 0.0063 | 0.0219 | –0.00322 | 0.00435 | 1.01 |
| | C11···H8–C8 (C–H···π) | 3.04, 130.5 | | 3.385 | 0.0043 | 0.0128 | –0.00203 | 0.00261 | 0.64 |
| | C8–H8···C11 | 3.04, 130.5 | | 3.385 | 0.0043 | 0.0128 | –0.00203 | 0.00261 | 0.64 |
| | C11–H11···N1 | 3.12, 119.9 | | 3.230 | 0.0035 | 0.0115 | –0.00184 | 0.00235 | 0.58 |
| | N1···H11–C11 | 3.12, 119.9 | | 3.230 | 0.0035 | 0.0115 | –0.00184 | 0.00235 | 0.58 |
| | Br1···H3–C3 | 3.31, 123.2 | | 3.354 | 0.0041 | 0.0126 | –0.00184 | 0.00249 | 0.58 |
| | C3–H3···Br1 | 3.31, 123.2 | | 3.354 | 0.0041 | 0.0126 | –0.00184 | 0.00249 | 0.58 |
| | | | | | | | | | |
| 3 | N1···H11–C11 | 2.66 149.6 | –7.0/–3.05 | 2.692 | 0.0073 | 0.0217 | –0.00418 | 0.00481 | 1.32 |
| | C11–H11···N1 | 2.66, 149.6 | | 2.692 | 0.0073 | 0.0217 | –0.00418 | 0.00481 | 1.32 |
| | C11–H11···H3–C3 | 2.31 | | 2.525 | 0.0060 | 0.0225 | –0.00367 | 0.00464 | 1.16 |
| | C3–H3···H11–C11 | 2.31 | | 2.525 | 0.0060 | 0.0225 | –0.00367 | 0.00464 | 1.16 |
| | C10–H10···H10–C10 | 2.28 | | 2.318 | 0.0057 | 0.0162 | –0.00305 | 0.00355 | 0.96 |
| | C8–H8···H10–C10 | 2.40 | | 2.445 | 0.0044 | 0.0136 | –0.00240 | 0.00289 | 0.76 |
| | C10–H10···H8–C8 | 2.40 | | 2.445 | 0.0044 | 0.0136 | –0.00240 | 0.00289 | 0.76 |
| | | | | | | | | | |
| 4 | C5–H5···N2 | 2.67, 117.4 | –5.7/–4.47 | 2.730 | 0.0076 | 0.0257 | –0.00435 | 0.00539 | 1.37 |
| | N2···H5–C5 | 2.67, 117.4 | | 2.730 | 0.0076 | 0.0258 | –0.00436 | 0.00540 | 1.37 |
| | C6–H6···N2 | 2.69, 118.0 | | 2.764 | 0.0070 | 0.0240 | –0.00400 | 0.00500 | 1.26 |
| | N2···H6–C6 | 2.69, 118.0 | | 2.764 | 0.0070 | 0.0240 | –0.00400 | 0.00500 | 1.26 |
| | | | | | | | | | |
| 5 | N2···H5–C5 | 2.88, 113.9 | –3.6/–2.96 | 2.993 | 0.0050 | 0.0168 | –0.00268 | 0.00344 | 0.84 |
| | C5–H5···N2 | 2.88, 113.9 | | 2.993 | 0.0050 | 0.0168 | –0.00267 | 0.00344 | 0.84 |
| | | | | | | | | | |
| 6 | C13···H13–C13 | 2.66, 173.6 | –3.2/–1.80 | 2.859 | 0.0075 | 0.0236 | –0.0038 | 0.00487 | 1.21 |
| | N2···Br1 | 3.49 | | 3.511 | 0.0051 | 0.0175 | –0.0027 | 0.00352 | 0.84 |
| | C14–H14···Br1 | 3.45, 115.0 | | 3.609 | 0.0033 | 0.0108 | –0.0014 | 0.00207 | 0.45 |
| | | | | | | | | | |
| 7 | C4–H4···Br1 | 3.59, 117.5 | -1.6/-0.71 | 3.634 | 0.0025 | 0.0087 | -0.0012 | 0.00167 | 0.37 |
| | C5–H5···Br1 | 3.11, 139.9 | | 3.030 | 0.0058 | 0.0188 | -0.0029 | 0.00378 | 0.90 |

**Table S6** Topological parameters for selected molecular pairs in **3H.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C2···C8 | 3.30 | –7.4/–5.87 | 3.356 | 0.0065 | 0.0180 | –0.00307 | 0.00378 | 0.97 |
| | C8···C11 | 3.42 | | 3.912 | 0.0058 | 0.0171 | –0.00273 | 0.00351 | 0.86 |
| | C9···C12 (π···π) | 3.43 | | 3.530 | 0.0058 | 0.0163 | –0.00270 | 0.00338 | 0.85 |
| | C4···C1 (π···π) | 3.48 | | 3.501 | 0.0048 | 0.0137 | –0.00225 | 0.00283 | 0.71 |
| | | | | | | | | | |
| 2 | C8–H8···N1 | 2.39, 167.6 | –6.3/–4.65 | 2.406 | 0.0133 | 0.0389 | –0.00745 | 0.00858 | 2.35 |
| | C2–H2···N1 | 2.46, 159.6 | | 2.487 | 0.0116 | 0.0332 | –0.00648 | 0.00740 | 2.04 |
| | C10–H10···N1 | 2.83, 143.2 | | 2.861 | 0.0054 | 0.0160 | –0.00298 | 0.00348 | 0.94 |
| | | | | | | | | | |
| 3 | N2···H13–C13 | 2.57, 137.5 | –5.5/–4.48 | 2.602 | 0.0080 | 0.0257 | –0.00439 | 0.00541 | 1.38 |
| | C13–H13···N2 | 2.57, 137.5 | | 2.602 | 0.0080 | 0.0257 | –0.00439 | 0.00541 | 1.38 |
| | C14–H14···H13–C13 | 2.49 | | 2.552 | 0.0040 | 0.0136 | –0.00223 | 0.00281 | 0.70 |
| | C13–H13···H14–C14 | 2.49 | | 2.552 | 0.0040 | 0.0136 | –0.00224 | 0.00281 | 0.70 |
| | | | | | | | | | |
| 4 | N2···H5–C5 | 2.56, 146.1 | –4.6/–3.14 | 2.587 | 0.0079 | 0.0247 | –0.00430 | 0.00524 | 1.35 |
| | C5–H5···N2 | 2.56, 146.1 | | 2.587 | 0.0079 | 0.0247 | –0.00430 | 0.00524 | 1.35 |
| | | | | | | | | | |
| 5 | N2···H6–C6 | 2.98, 111.3 | –3.6/–2.89 | 3.137 | 0.0042 | 0.0148 | –0.00227 | 0.00298 | 0.72 |
| | C6–H6···N2 | 2.98, 111.3 | | 3.137 | 0.0042 | 0.0148 | –0.00227 | 0.00298 | 0.72 |

**Table S7** Topological parameters for selected molecular pairs in **3F.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C15···C7 | 3.32 | –6.3/5.22 | 3.522 | 0.0064 | 0.0197 | –0.00323 | 0.00408 | 1.02 |
| | C14···C9 (π···π) | 3.43 | | 3.501 | 0.0058 | 0.0154 | –0.00267 | 0.00326 | 0.84 |
| | C12···C11 (π···π) | 3.42 | | 3.521 | 0.0056 | 0.0152 | –0.00251 | 0.00315 | 0.79 |
| | C1···C2 (π···π) | 3.51 | | 3.710 | 0.0053 | 0.0138 | –0.00242 | 0.00294 | 0.76 |
| | N1···C4 (π···π) | 3.51 | | 4.137 | 0.0044 | 0.0128 | –0.00212 | 0.00266 | 0.67 |
| | | | | | | | | | |
| 2 | C6–H6···N2 | 2.54, 152.4 | –6.0/–1.69 | 2.565 | 0.0086 | 0.0270 | –0.14959 | 0.00479 | 1.51 |
| | C8–H8···N2 | 2.45, 165.0 | | 2.465 | 0.0106 | 0.0335 | -0.07017 | 0.00592 | 1.87 |
| | C10–H10···N2 | 2.79, 146.7 | | 2.812 | 0.0055 | 0.0168 | -0.28260 | 0.00301 | 0.95 |
| | | | | | | | | | |
| 3 | C2–H2···H6–C6 | 2.39 | –5.8/–3.42 | 2.497 | 0.0058 | 0.0190 | –0.00313 | 0.00393 | 0.98 |
| | C8···N2 | 3.32 | | 3.602 | 0.0054 | 0.0188 | –0.00288 | 0.00379 | 0.91 |
| | | | | | | | | | |
| 4 | C4–H4···N1 | 2.51, 140.2 | –2.5/–1.29 | 2.532 | 0.0109 | 0.0313 | –0.00600 | 0.00691 | 1.89 |
| | | | | | | | | | |
| 5 | C11–H11···F1 | 2.43, 155.5 | –2.2/–2.01 | 2.444 | 0.0077 | 0.0293 | –0.00546 | 0.00639 | 1.72 |
| | F1···H11–C11 | 2.43, 155.5 | | 2.445 | 0.0077 | 0.0293 | –0.00546 | 0.00639 | 1.72 |
| | | | | | | | | | |
| 6 | C13–H13···F1 | 2.51, 143.6 | -2.0/-1.60 | 2.537 | 0.0064 | 0.0252 | -0.00459 | 0.00545 | 1.45 |
| | C13–H13···F1 | 2.51, 143.6 | | 2.537 | 0.0064 | 0.0252 | -0.00459 | 0.00545 | 1.44 |
| | F1···F1 | 3.39 | | 3.393 | 0.0020 | 0.0138 | -0.00154 | 0.00249 | 0.49 |

**Table S8** Topological parameters for selected molecular pairs in **3Cl.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal/mol) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C2···C8 | 3.25 | –8.4/–7.15 | 3.272 | 0.0070 | 0.0206 | –0.00345 | 0.00430 | 1.09 |
| | C7···C14 | 3.36 | | 3.383 | 0.0065 | 0.0184 | –0.00316 | 0.00388 | 1.00 |
| | C9···C12 (π···π) | 3.42 | | 3.445 | 0.0055 | 0.0163 | –0.00278 | 0.00343 | 0.88 |
| | C14···Cl1 | 3.64 | | 3.675 | 0.0052 | 0.0164 | –0.00251 | 0.00331 | 0.79 |
| | C4···C1 (π···π) | 3.52 | | 3.558 | 0.0045 | 0.0127 | –0.00210 | 0.00264 | 0.66 |
| | | | | | | | | | |
| 2 | C2–H2···N1 | 2.46, 165.5 | –6.1/–4.49 | 2.479 | 0.0116 | 0.0328 | –0.00639 | 0.00730 | 2.01 |
| | C8–H8···N1 | 2.52, 164.3 | | 2.537 | 0.0105 | 0.0296 | –0.00579 | 0.00659 | 1.82 |
| | C10–H10···N1 | 2.85, 150.1 | | 2.881 | 0.0052 | 0.0150 | –0.00282 | 0.00328 | 0.89 |
| | | | | | | | | | |
| 3 | C10–H10···N2 | 2.76, 109.2 | –4.5/–3.08 | 2.892 | 0.0070 | 0.0244 | –0.00393 | 0.00501 | 1.24 |
| | Cl1···H5–C5 | 3.06, 132.1 | | 3.093 | 0.0048 | 0.0156 | –0.00228 | 0.00308 | 0.72 |
| | | | | | | | | | |
| 4 | C11–H11···N2 | 2.55, 148.7 | –2.8/–2.67 | 2.569 | 0.0082 | 0.0254 | –0.00439 | 0.00536 | 1.38 |

**Table S9** Topological parameters for selected molecular pairs in **3Br.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C14···C7 | 3.36 | –7.6/–7.25 | 3.407 | 0.0065 | 0.0189 | –0.00317 | 0.00395 | 1.00 |
| | C8···C2 | 3.31 | | 3.337 | 0.0064 | 0.0188 | –0.00313 | 0.00391 | 0.98 |
| | Br1···C14 | 3.75 | | 4.011 | 0.0054 | 0.0159 | –0.00253 | 0.00326 | 0.80 |
| | Br1···C10 | 3.76 | | 3.860 | 0.0053 | 0.0157 | –0.00252 | 0.00322 | 0.79 |
| | C12···C9 (π···π) | 3.50 | | 3.548 | 0.0050 | 0.0146 | –0.00246 | 0.00305 | 0.77 |
| | C1···C4 (π···π) | 3.57 | | 3.642 | 0.0042 | 0.0117 | –0.00195 | 0.00244 | 0.61 |
| | | | | | | | | | |
| 2 | C2–H2···N1 | 2.47, 166.2 | –6.1/–4.56 | 2.486 | 0.0114 | 0.0323 | –0.00630 | 0.00719 | 1.98 |
| | C8–H8···N1 | 2.51, 164.0 | | 2.530 | 0.0106 | 0.0300 | –0.00587 | 0.00669 | 1.85 |
| | | | | | | | | | |
| 3 | C10–H10···N2 | 2.79, 108.3 | –3.9/–2.99 | 2.938 | 0.0067 | 0.0236 | –0.00378 | 0.00484 | 1.19 |
| | | | | | | | | | |
| 4 | C11–H11···N2 | 2.54, 147.9 | –2.7/–1.43 | 2.563 | 0.0083 | 0.0259 | –0.00448 | 0.00548 | 1.41 |
| | | | | | | | | | |
| 5 | C5–H5···Br1 | 4.08, 134.5 | –2.4/–1.30 | 3.285 | 0.0044 | 0.0128 | -0.00196 | 0.00258 | 0.62 |
| | C13–H13···C5 | 4.01,155.1 | | 3.037 | 0.0040 | 0.0109 | -0.00188 | 0.00230 | 0.59 |

**Table S10** Topological parameters for selected molecular pairs in **4Cl.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C8···C15 | 3.32 | –8.0/–6.43 | 3.400 | 0.0063 | 0.0195 | –0.00316 | 0.00402 | 1.00 |
| | C12···C13 (π···π) | 3.43 | | 3.602 | 0.0058 | 0.0156 | –0.00272 | 0.00332 | 0.86 |
| | C10···C9 (π···π) | 3.43 | | 3.524 | 0.0059 | 0.0156 | –0.00271 | 0.00331 | 0.85 |
| | C2···C6 (π···π) | 3.50 | | 3.781 | 0.0058 | 0.0151 | –0.00265 | 0.00322 | 0.84 |
| | C3···C5 (π···π) | 3.48 | | 3.563 | 0.0050 | 0.0144 | –0.00238 | 0.00300 | 0.75 |
| | Cl1···Cl1 | 3.83 | | 3.834 | 0.0041 | 0.0140 | –0.00181 | 0.00266 | 0.57 |
| | | | | | | | | | |
| 2 | C2–H2···N2 | 2.89, 113.3 | –5.6/–3.00 | 2.966 | 0.0052 | 0.0171 | -0.00279 | 0.00353 | 0.88 |
| | | | | | | | | | |
| 3 | C10–H10···N2 | 2.58, 149.2 | –5.2/–3.88 | 2.611 | 0.0080 | 0.0245 | –0.00436 | 0.00524 | 1.37 |
| | C8–H8···N2 | 2.60, 155.5 | | 2.622 | 0.0079 | 0.0240 | –0.00436 | 0.00518 | 1.37 |
| | C2–H2···N2 | 2.91, 161.8 | | 2.958 | 0.0041 | 0.0134 | –0.00229 | 0.00281 | 0.72 |
| | | | | | | | | | |
| 4 | N1···H3–C3 | 2.69, 138.2 | –2.7/–2.16 | 2.719 | 0.0072 | 0.0202 | –0.00398 | 0.00452 | 1.25 |
| | C5···N1 | 3.50 | | 3.881 | 0.0044 | 0.0151 | –0.00236 | 0.00306 | 0.74 |
| | | | | | | | | | |
| 5 | C5–H5···N1 | 2.42, 166.3 | –2.5/-2.12 | 2.440 | 0.0121 | 0.0350 | –0.00650 | 0.00762 | 2.05 |
| | | | | | | | | | |
| 6 | Cl1···Cl1 | 3.59 | –2.2/-2.47 | 3.588 | 0.0064 | 0.0230 | –0.00300 | 0.00438 | 0.94 |
| | C11–H11···Cl1 | 3.10, 144.8 | | 3.039 | 0.0048 | 0.0159 | –0.00236 | 0.00316 | 0.74 |

**Table S11** Topological parameters for selected molecular pairs in **4Br.**

| Dimer | Atoms | Geometry *(Å, °)* | PIXEL/DFT (kcal mol$^{-1}$) | $R_{ij}$ (Å) | ρ (e/Å$^3$) | $\nabla^2\rho$ (e/Å$^5$) | V (a.u.) | G (a.u.) | $E_{HB}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C6···C12 (π···π) | 3.50 | –10.6/–9.54 | 3.761 | 0.0057 | 0.0151 | –0.00258 | 0.00318 | 0.81/0.86 |
| | C12···C6 (π···π) | 3.50 | | 3.761 | 0.0057 | 0.0151 | –0.00258 | 0.00318 | 0.81/0.86 |
| | Br1···C5 | 3.68 | | 3.898 | 0.0051 | 0.0174 | –0.00241 | 0.00337 | 0.76/0.91 |
| | C5···Br1 | 3.68 | | 3.898 | 0.0051 | 0.0173 | –0.00241 | 0.00337 | 0.76/0.91 |
| | C9···C7 | 3.55 | | 3.567 | 0.0045 | 0.0129 | –0.00218 | 0.00270 | 0.69/0.73 |
| | C7···C9 | 3.55 | | 3.567 | 0.0045 | 0.0129 | –0.00218 | 0.00270 | 0.69/0.73 |
| | C1···C14 (π···π) | 3.63 | | 3.661 | 0.0043 | 0.0114 | –0.00202 | 0.00244 | 0.64/0.66 |
| | C14···C1 (π···π) | 3.63 | | 3.661 | 0.0043 | 0.0114 | –0.00202 | 0.00244 | 0.64/0.66 |
| | | | | | | | | | |
| 2 | Br1···C3 | 3.57 | –9.1/–7.57 | 3.586 | 0.0066 | 0.0201 | –0.00316 | 0.00409 | 0.99/1.11 |
| | C3···Br1 | 3.57 | | 3.586 | 0.0066 | 0.0201 | –0.00316 | 0.00409 | 0.99/1.11 |
| | C12···C2 (π···π) | 3.48 | | 3.616 | 0.0056 | 0.0157 | –0.00266 | 0.00329 | 0.84/0.89 |
| | C2···C12 (π···π) | 3.48 | | 3.616 | 0.0056 | 0.0157 | –0.00266 | 0.00329 | 0.84/0.89 |
| | C9···C8 | 3.54 | | 3.692 | 0.0049 | 0.0131 | –0.00230 | 0.00279 | 0.72/0.75 |
| | C8···C9 | 3.54 | | 3.692 | 0.0049 | 0.0131 | –0.00230 | 0.00279 | 0.72/0.75 |
| | C7···C11 | 3.65 | | 3.899 | 0.0042 | 0.0110 | –0.00199 | 0.00237 | 0.63/0.64 |
| | C11···C7 | 3.65 | | 3.900 | 0.0042 | 0.0110 | –0.00199 | 0.00237 | 0.63/0.64 |
| | | | | | | | | | |
| 3 | N1···H2–C2 | 2.46, 167.4 | –5.3/–3.18 | 2.482 | 0.0113 | 0.0322 | –0.00619 | 0.00712 | 1.95/1.92 |
| | C3–H3···H10–C10 | 2.01 | | 2.062 | 0.0107 | 0.0338 | –0.00591 | 0.00719 | 1.86/1.94 |
| | N1···H8–C8 | 2.78, 163.3 | | 2.819 | 0.0066 | 0.0185 | –0.00364 | 0.00413 | 1.15/1.12 |
| | | | | | | | | | |
| 4 | C11–H11···H11–C11 | 2.19 | –3.8/–1.63 | 2.287 | 0.0090 | 0.0301 | –0.00497 | 0.00624 | 1.57/1.69 |
| | C11–H11···Br1 | 3.26, 120.1 | | 3.328 | 0.0045 | 0.0150 | –0.00223 | 0.00298 | 0.70/0.81 |
| | Br1···H11–C11 | 3.26, 120.1 | | 3.328 | 0.0045 | 0.0150 | –0.00223 | 0.00298 | 0.70/0.81 |
| | | | | | | | | | |
| 5 | C13–H13···N2 | 2.57,157.5 | –3.5/–2.47 | 2.583 | 0.0082 | 0.0249 | -0.00440 | 0.00531 | 1.39/1.43 |
| | Br1···H14–C14 | 3.11, 124.9 | | 3.148 | 0.0052 | 0.0169 | -0.00259 | 0.00340 | 0.82/0.92 |
| | Br1···N2 | 3.76 | | 3.764 | 0.0041 | 0.0125 | -0.00187 | 0.00250 | 0.59/0.68 |
| | | | | | | | | | |
| 6 | C3–H3···N2 | | –3.3/–2.47 | 2.980 | 0.0043 | 0.0136 | -0.00228 | 0.00284 | 0.72/0.77 |

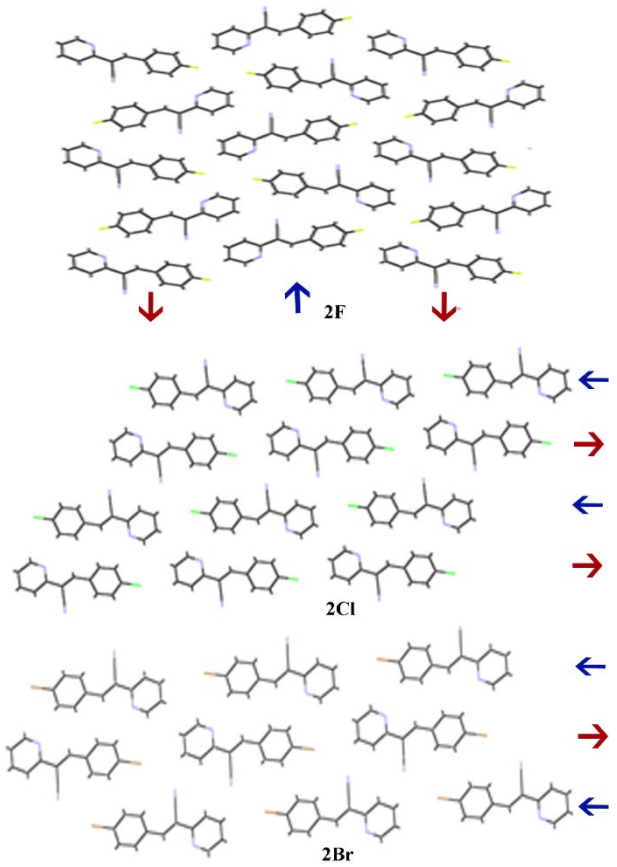


**Fig. S24** Arrangement of molecular layers in **2py**. The highlighted arrows indicate the orientation of nitrile group.

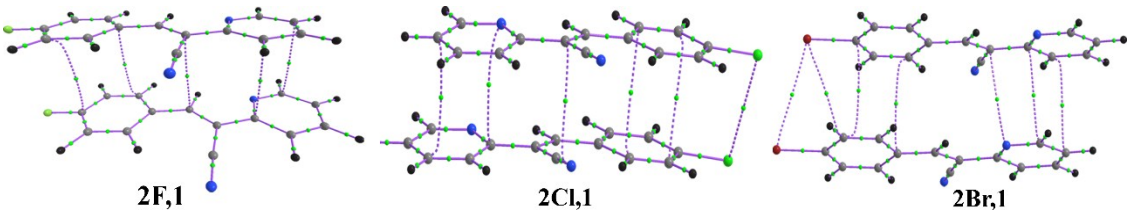


**Fig. S25** The molecular graphs showing homo parallel π···π interactions (**1**) in **2F**, **2Cl**, and **3Br**.

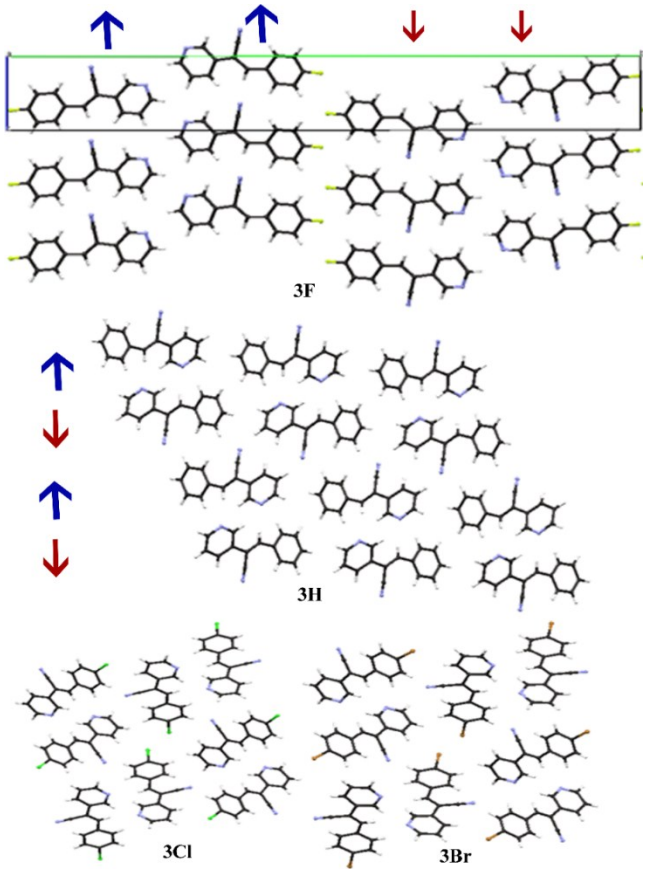


**Fig. S26** Arrangement of molecular layers in **3py**. The highlighted arrows indicate the orientation of nitrile group.

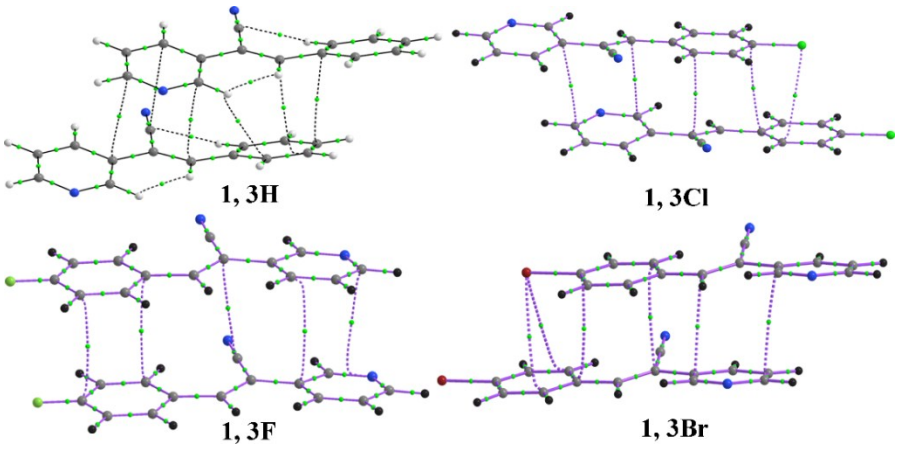


**Fig. S27** The molecular graphs showing homo parallel (**1,3F**) and slipped-parallel π···π interactions in **3H**, **3Cl**, and **3Br.**

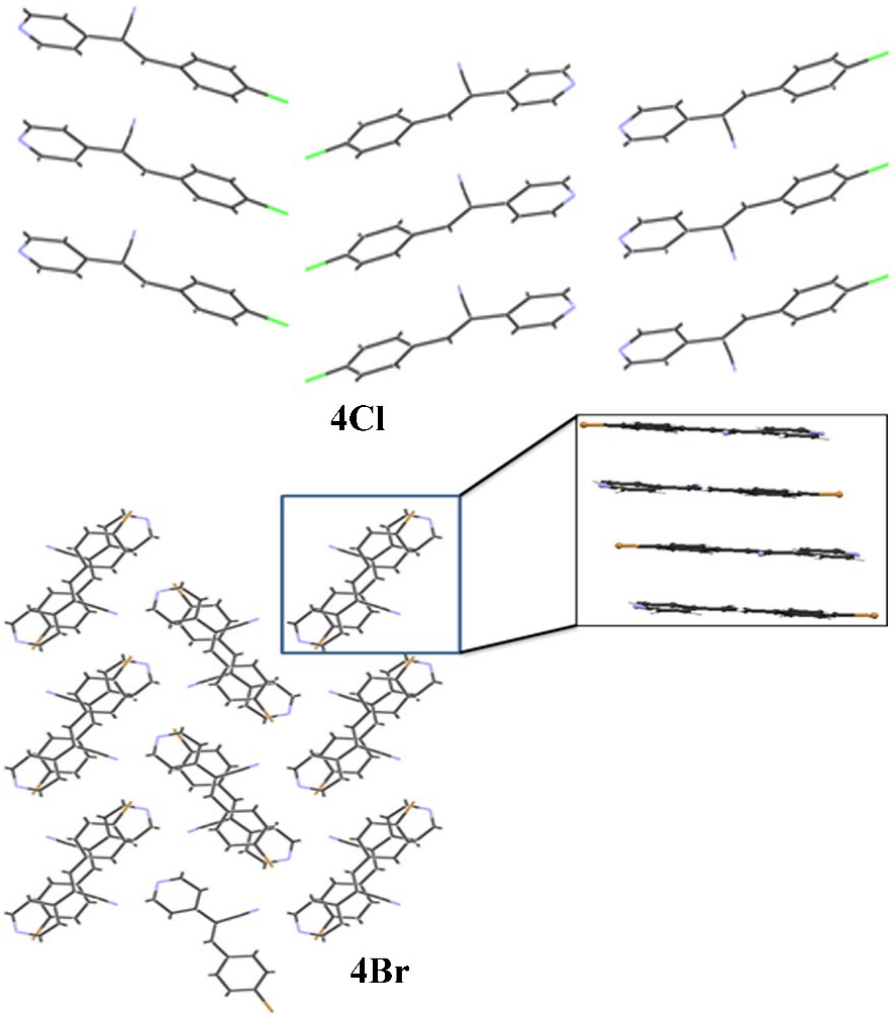


**Fig. S28** Arrangement of molecular layers in **4py**.

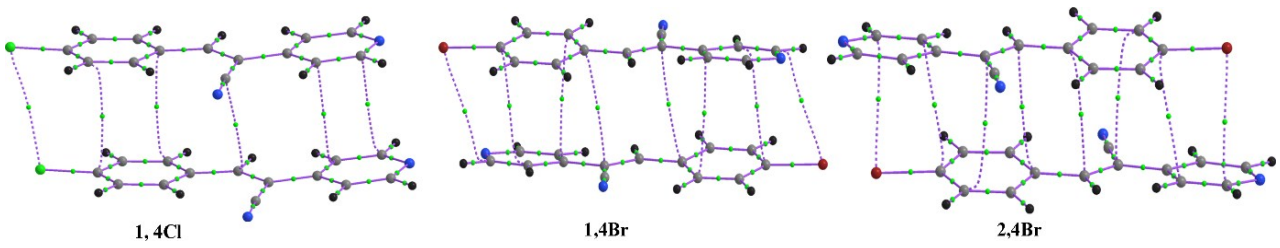


**Fig. S29** The molecular graphs showing the homo parallel π···π interactions in **4Cl**, hetero π···π interactions and π···Br interactions in **4Br**.

**Table S12** Lattice energies (in kcal mol$^{-1}$) partitioned into Coulombic, polarization, dispersion and repulsion contributions for title compounds.

| Family | Compound [a] | $E_{coul}$ | $E_{pol}$ | $E_{disp}$ (% $E_{disp}$) | $E_{rep}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| **2Py** | 2F | −2.3 | −4.9 | −32.3 (81.7) | 11.2 | −28.3 |
| | 2Cl | −1.5 | −4.5 | −35.1 (85.5) | 10.9 | −30.2 |
| | 2Br | −4.2 | −3.3 | −37.0 (83.1) | 13.2 | −31.3 |
| **3Py** | 3H | −5.7 | −3.7 | −31.1 (76.8) | 10.6 | −29.9 |
| | 3F | −5.8 | −4.3 | −33.3 (76.6) | 12.1 | −31.3 |
| | 3Cl | −4.5 | −3.8 | −35.9 (81.2) | 11.6 | −32.5 |
| | 3Br | −4.2 | −3.3 | −37.0 (83.1) | 13.2 | −31.3 |
| **4Py** | 4Cl | −4.1 | −4.3 | −36.9 (81.5) | 12.0 | −33.2 |
| | 4Br | −3.8 | −3.5 | −37.5 (83.8) | 14.0 | −30.8 |

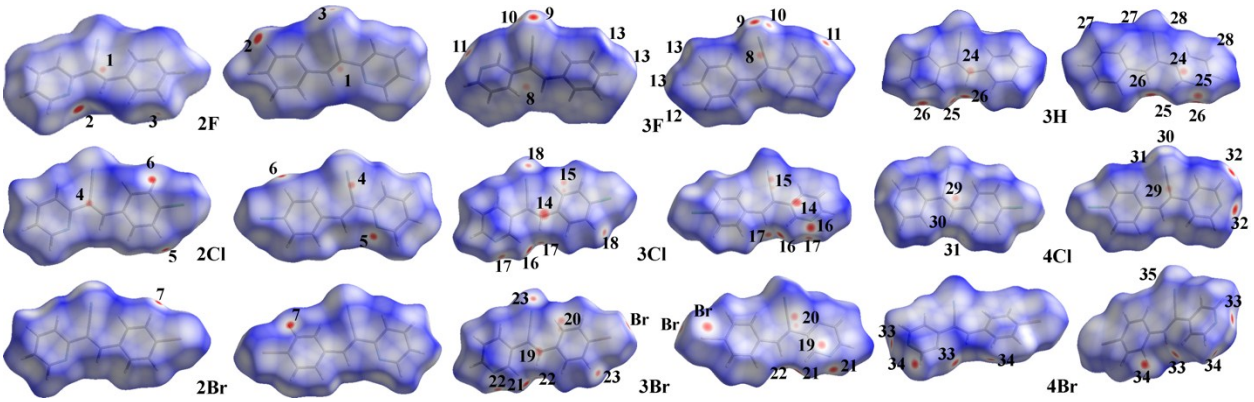


**Fig. S30** Two different views of Hirshfeld surfaces mapped with $d_{norm}$ and key intermolecular contacts are labelled (see Table 2 for interactions details)

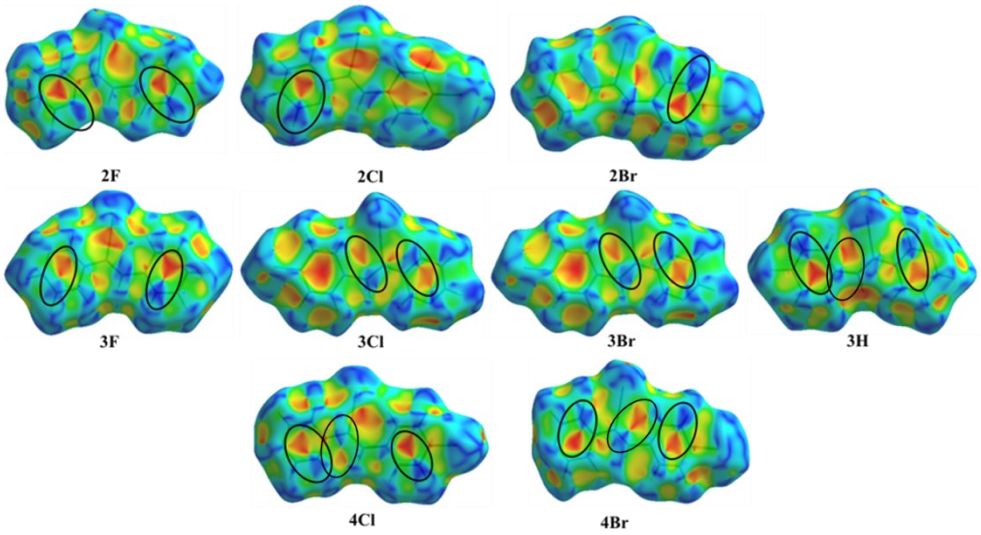


**Fig. S31** Red and blue triangles (circled) indicate the presence of π stacking interactions in the title compounds as evident from the shape index plots.

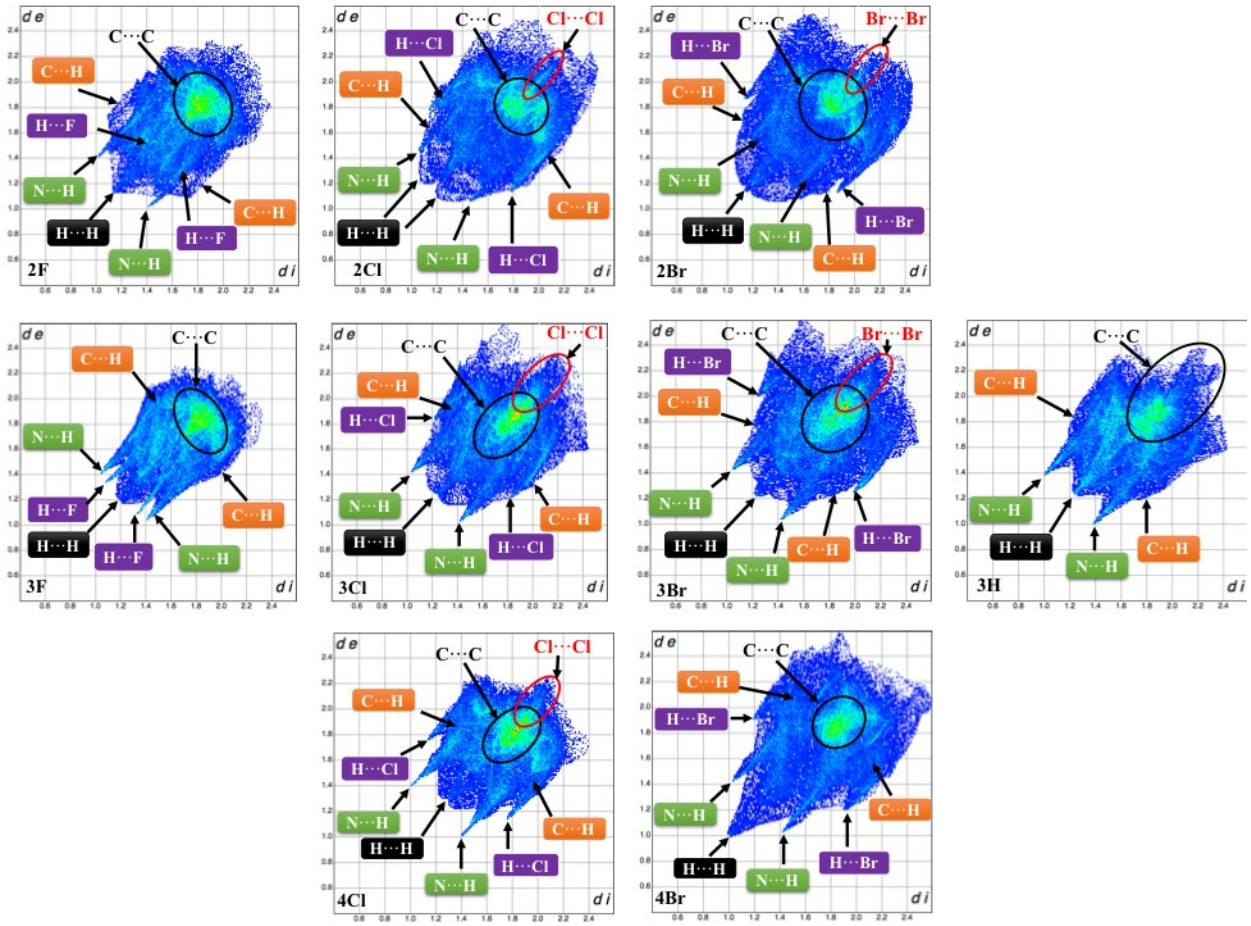


**Fig. S32** Two-dimensional fingerprint plots for title compounds showing different intermolecular contacts.

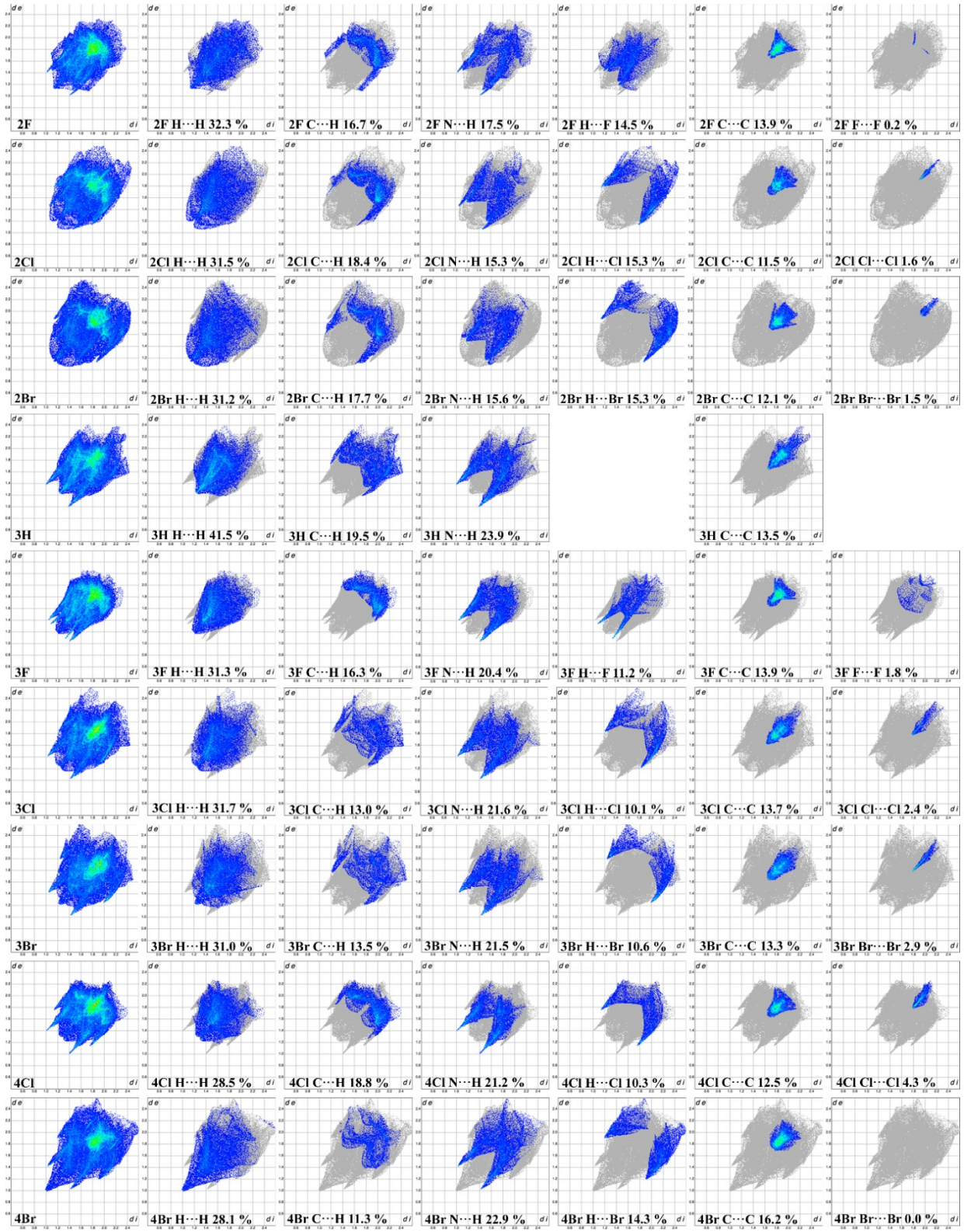


**Fig. S33** Decomposed two-dimensional fingerprint plots for title compounds and the relative contribution of various intermolecular contacts are shown.

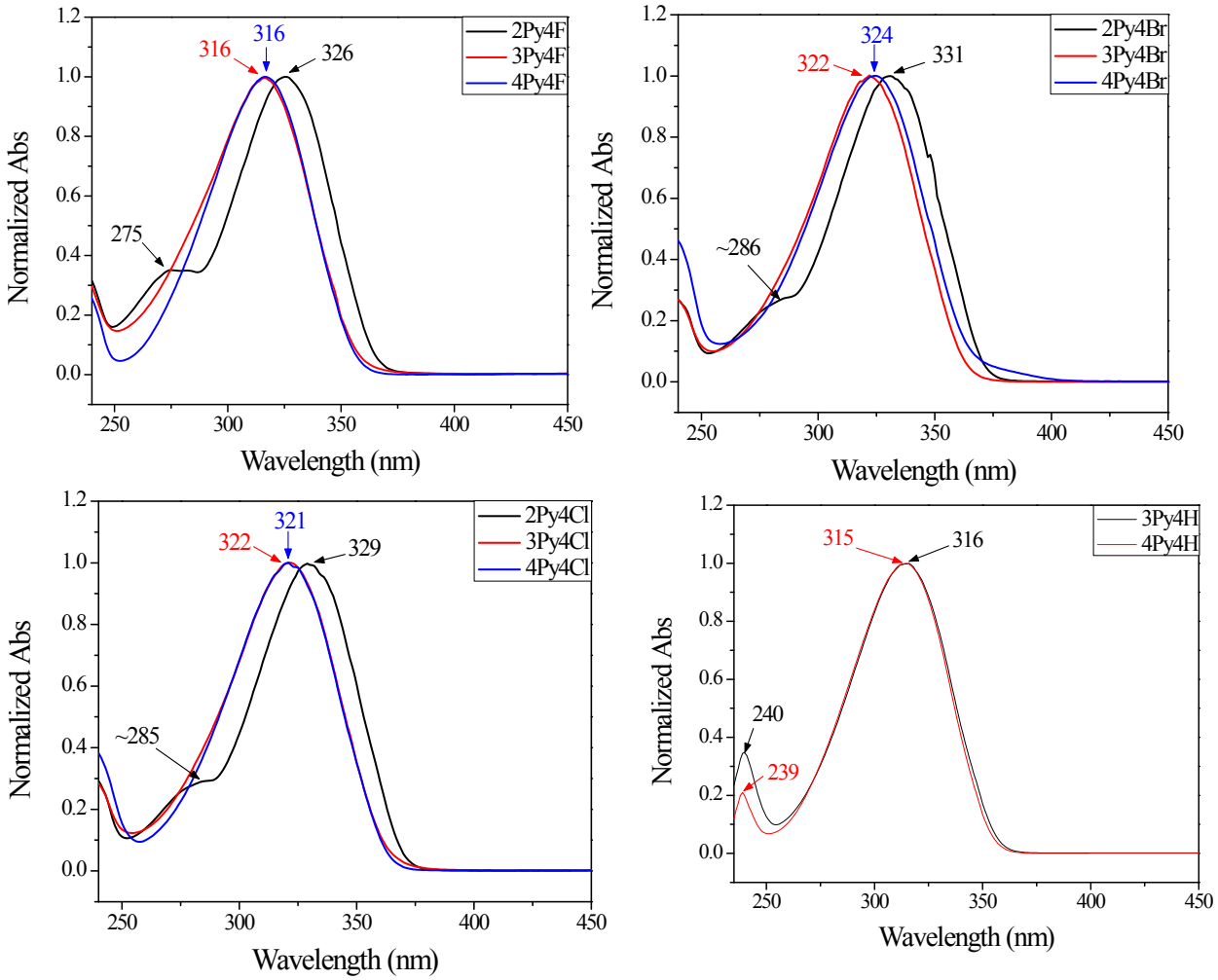


**Fig. S34** Normalized UV-Vis absorbance spectra of (*Z*)-3-(4-halophenyl)-2-(pyridin-2/3/4-yl)acrylonitrile derivatives in $CHCl_3$ (here, 2Py4F(**2F**), 3Py4F(**3F**) and 4Py4F (**4F**); 2Py4Cl(**2Cl**), 3Py4Cl(**3Cl**) and 4Py4Cl (**4Cl**); 2Py4Br(**2Br**), 3Py4Br(**3Br**) and 4Py4Br (**4Br**) and 2Py4H(**2H**), 3Py4H(**3H**) and 4Py4H (**4H**)).

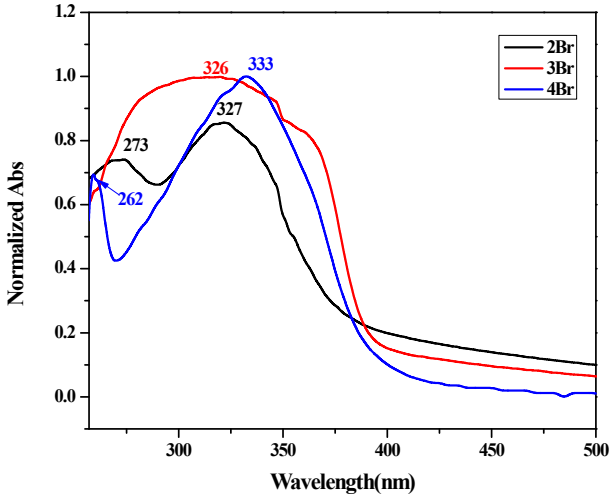


**Fig. S35** Normalized UV-Vis absorbance spectra of **2Br**, **3Br** and **4Br** in the solid state**.**

**Reference:**

1. Percino, M. J.; Chapela, V. M.; Pérez-Gutiérrez, E.; Cerón, M.; Soriano, G., Synthesis, optical, and spectroscopic characterisation of substituted 3-phenyl-2-arylacrylonitriles. *Chemical Papers* **2011,** *65* (1), 42-51.

2. Percino, M. J.; Chapela, V. M.; Montiel, L.-F.; Pérez-Gutiérrez, E.; Maldonado, J. L., Spectroscopic characterization of halogen- and cyano-substituted pyridinevinylenes synthesized without catalyst or solvent. *Chemical Papers* **2010,** *64* (3), 360-367.

3. Del Fiandra, C.; Moccia, M.; Cerulli, V.; Adamo, M. F. A., Catalytic asymmetric conjugate addition of isocyanoacetate to (Z)-3-substituted-2-(4-pyridyl)-acrylonitrile, a reactive class of Michael acceptor. *Chemical Communications* **2016,** *52* (8), 1697-1700.