## Electronic Supporting Information (ESI)

# Role of halogen atoms in the mechanical properties of para-substituted benzaldehyde oxime

*Priyasha Harsha,*[a] *and Dinabandhu Das* [*, a]

School of Physical Sciences, Jawaharlal Nehru University, New Delhi-110067, India

*Email: jnu.dinu@gmail.com*

**TABLE OF CONTENTS**


| | | |
|---|---|---|
| **1)** | **Experimental Section** | **S3** |
| | **a) FTIR Spectra** | |
| **2)** | **Powder X-Ray Diffraction Study** | **S4** |
| **3)** | **Thermogravimetric Analysis (TGA)** | **S5** |
| **4)** | **Differential scanning calorimetry (DSC)** | **S5-S6** |
| **5)** | **Crystal Morphology with Face indices** | **S6-S8** |
| **6)** | **Energy calculations figures and tables** | **S9-S11** |
| **7)** | **Unit cell parameters** | **S12** |
| **8)** | **H-Bonding parameters** | **S12** |
| **9)** | **Description of videos (Video S1, S2, S3 and S4)** | **S13** |
| **10)** | **References** | **S13** |

## 1. Experimental Section

**Synthesis:** All the respective aldehydes, hydroxylamine and sodium hydroxide were purchased from Sigma-Aldrich. After distillation, commercially available solvents such as ethanol, ethyl acetate and hexane were used. All the compounds were synthesized by their reported literature[1] and compounds are characterized by IR, PXRD and matched the unit cell parameters to confirm the structure by SCXRD. Transmission infrared spectra of the solids were obtained using a Fourier–transform infrared spectrometer (Shimadzu), and 43 scans were collected at 4 $cm^{-1}$ resolution for each sample. The spectra were measured over the range of 4000-400 $cm^{-1}$.

### a) FTIR Spectra

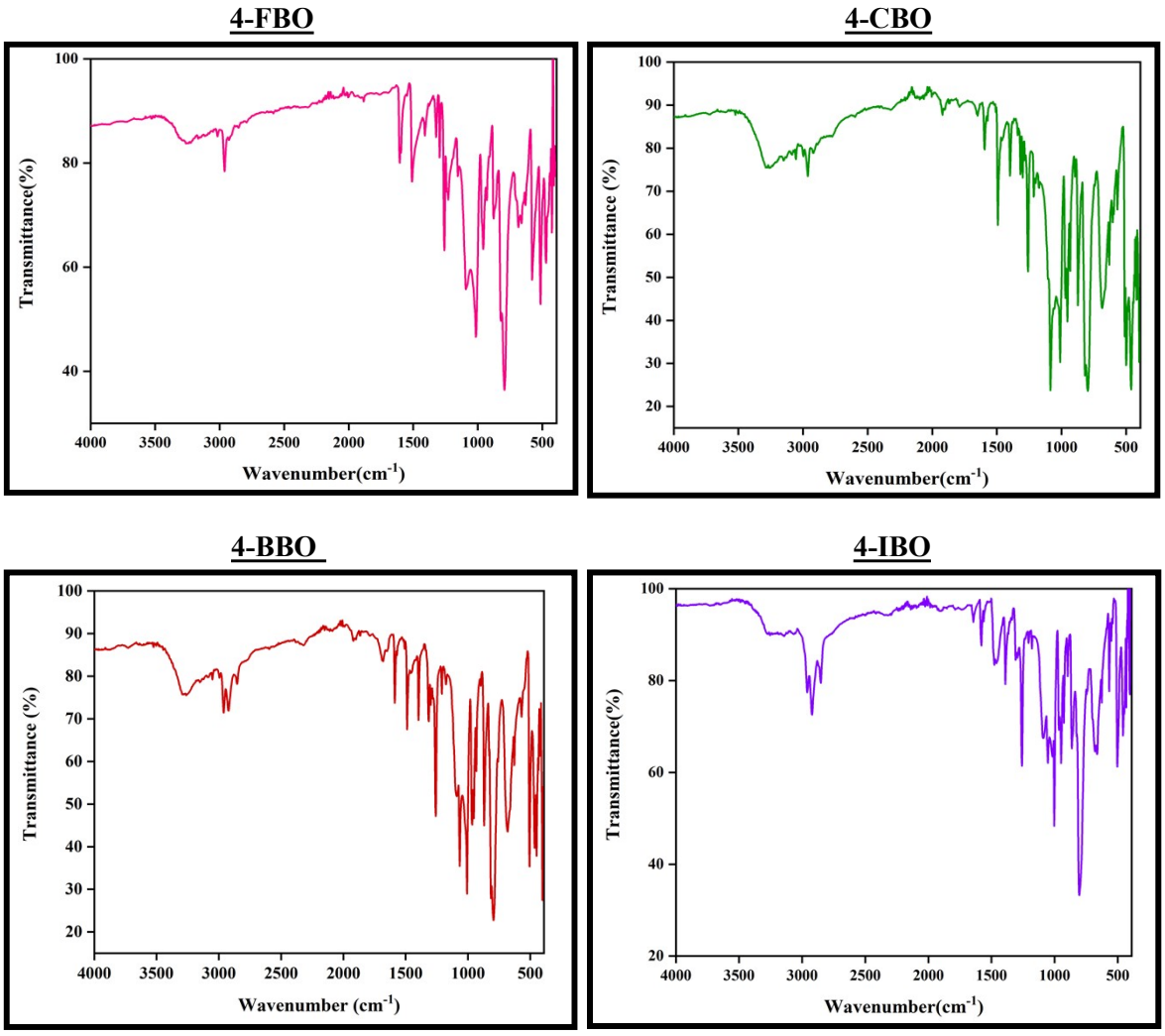



**Figure S1**: IR spectrum of *p*-substituted benzaldehyde oxime (indicates the formation of product by the O–H stretching(3200-3550$cm^{-1}$) and C=N stretching(1690-1640$cm^{-1}$)

## 2. Powder XRD Diffraction Patterns:

Powder X-ray diffractogram was measured on a Rigaku powder X-ray diffractometer (Miniflex600 with Cu Kα radiation, λ = 1.54059 Å) operating in Bragg−Brentano geometry. Crystals of the compound were crushed gently and layered on a sample holder. Data were recorded at room temperature at a scan rate of 2°/min from 5° to 40° (2θ value).

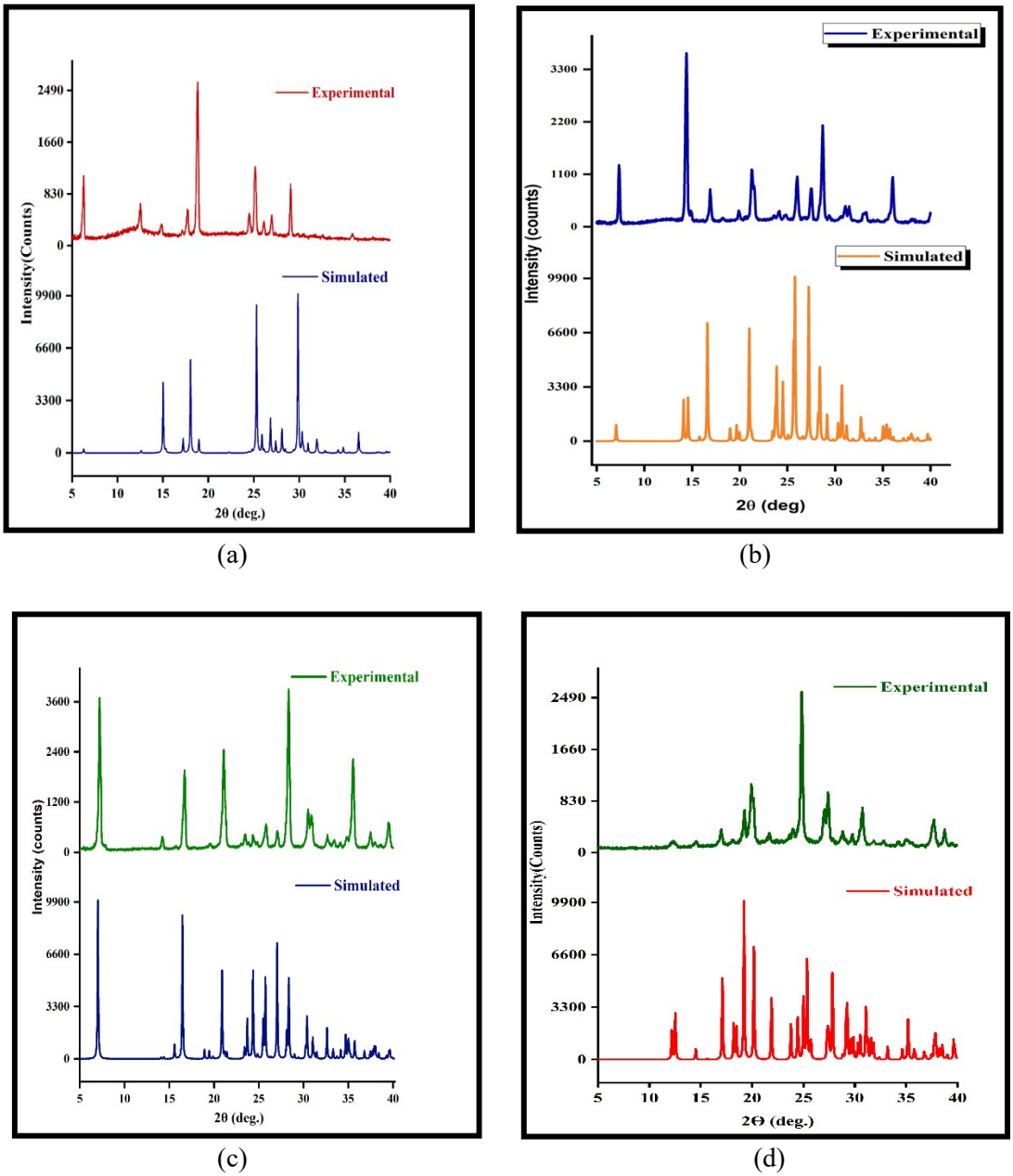



**Figure S2**: Experimental and simulated PXRD pattern of (a) **4-FBO**, (b**) 4-CBO**, (c) **4-BBO** and (d) **4-IBO**

## 3. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measurement was done in Mettler Toledo instrument supported with StarRe software version 13.00 with a heating rate of 5℃/min.

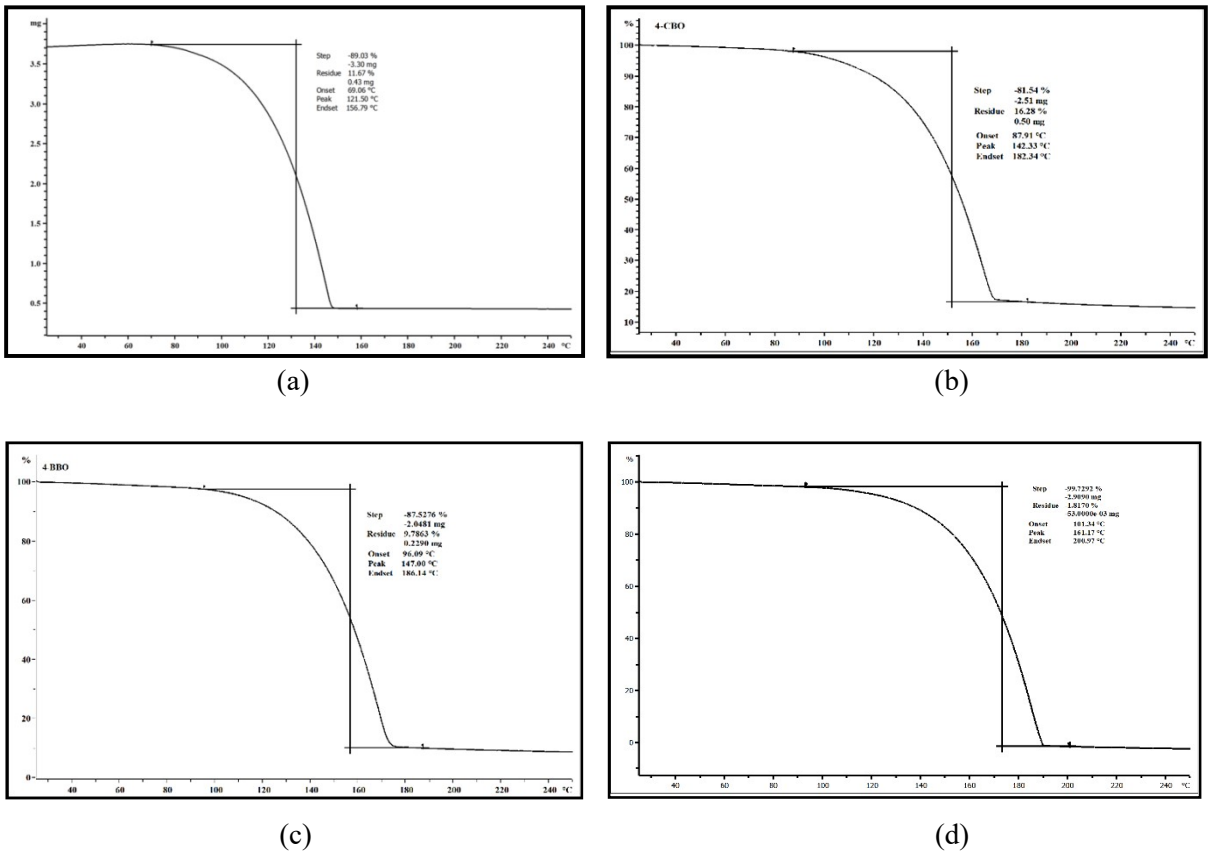



**Figure S3:** TGA thermogram shows mass loss of (a) **4-FBO,** (b) **4-CBO**, (c) **4-BBO and** (d) **4-IBO**

## 4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 calorimeter with FRS5 DSC Sensor attached to a HUBER TC100-MT chiller and STARe software v 13.00. Pure crystalline powder was sealed in an aluminium pan and covered with a pierced lid. Samples were heated at the rate of 10°C/min under the flow of N2 gas at the rate of 20 ml/min.

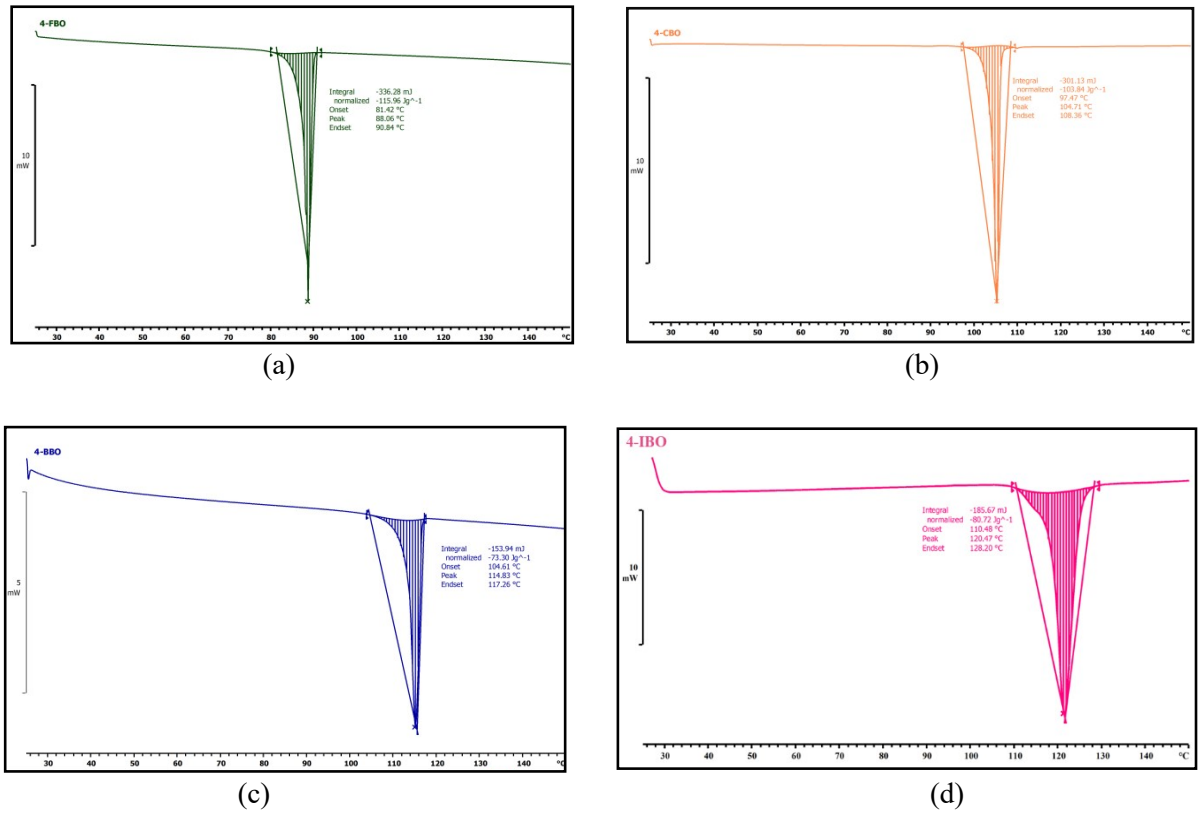



**Figure S4:** DSC thermograms show the melting point of (a) **4-FBO** (88˚C)**,** (b) **4-CBO** (104˚C)**,** (c) **4-BBO** (114˚C) **and** (d) **4-IBO** (120˚C).

## 5. Crystal Morphology with Face indices

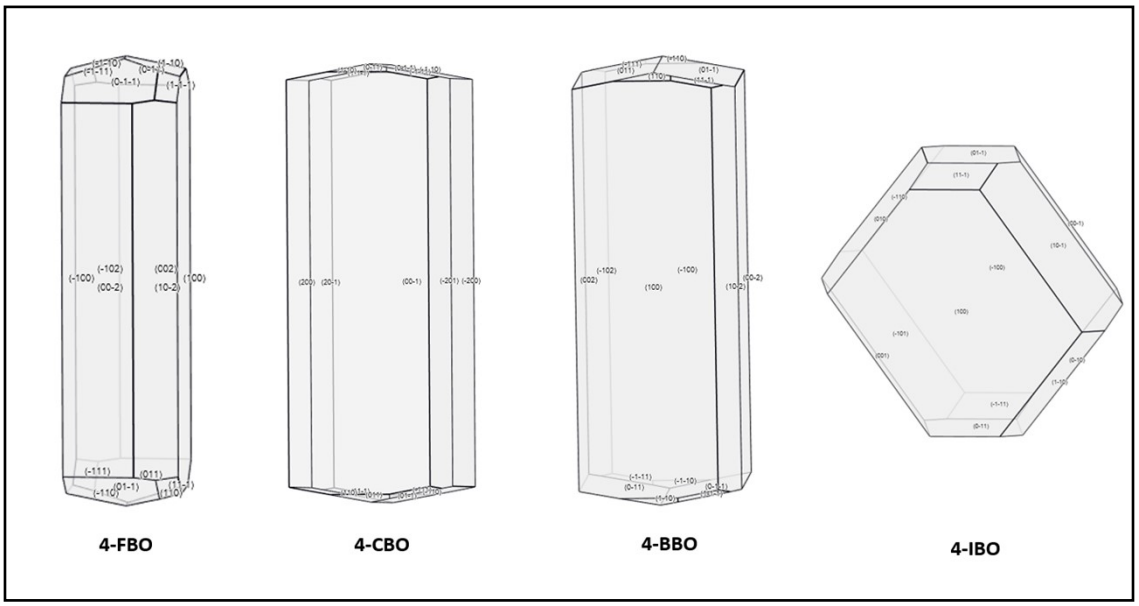
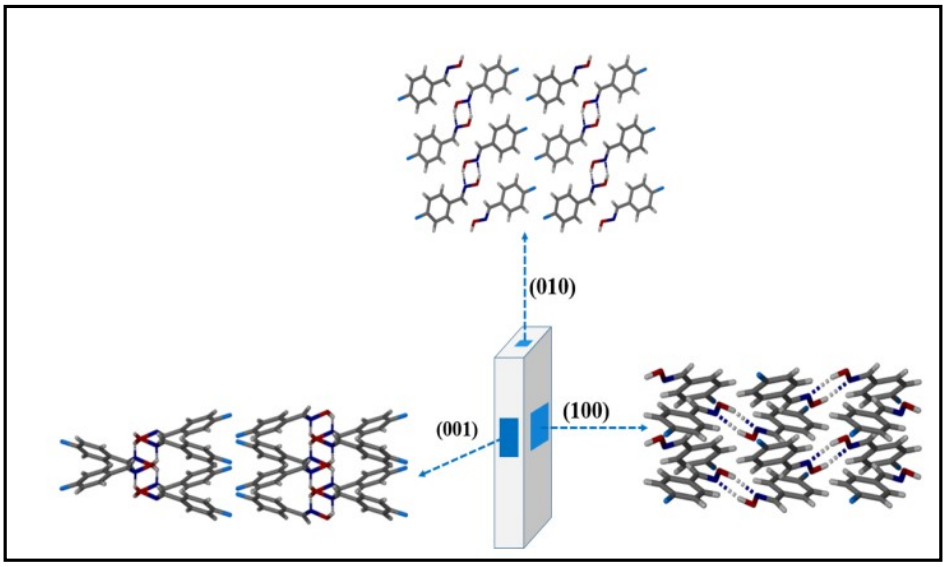
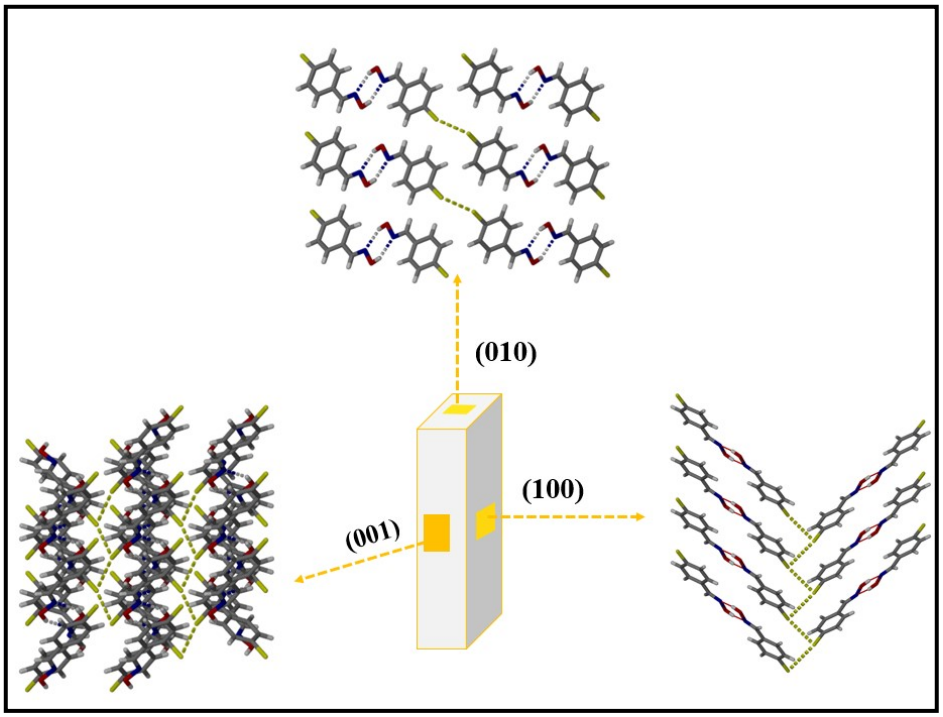


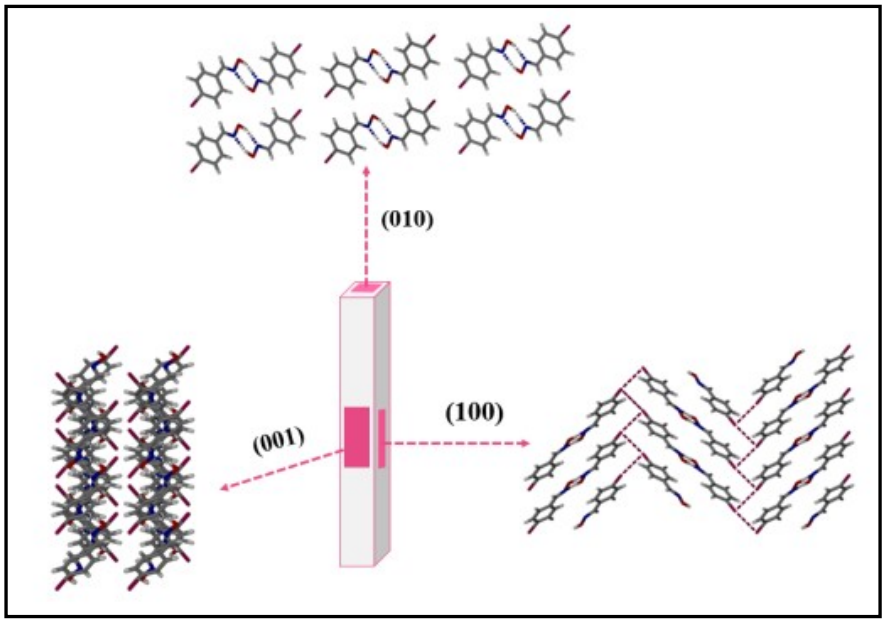

**Figure S5:** Face indices of all compounds determined using BFDH morphology in Mercury software.[2]



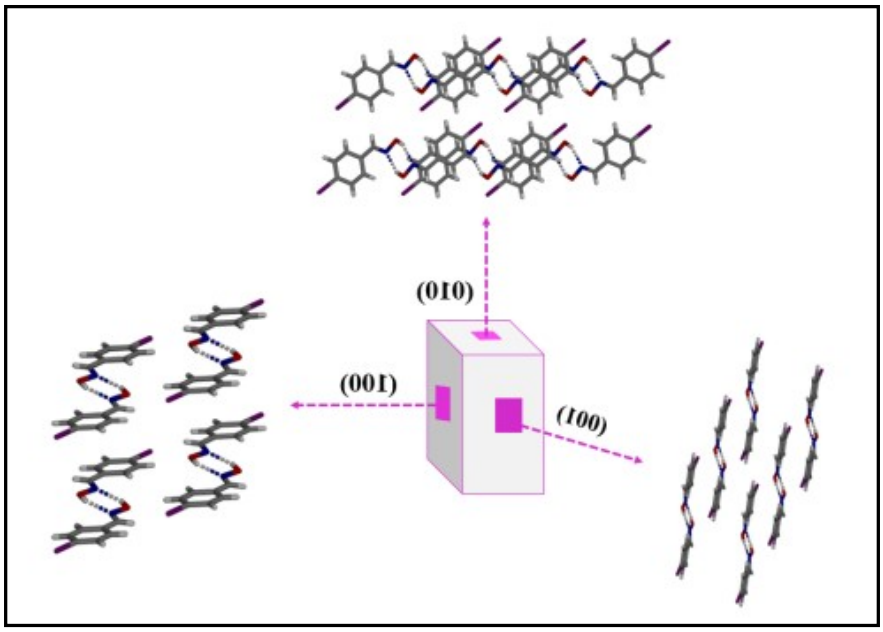

(a)




(b)




(c)




(d)

**Figure S6:** Crystal morphology with face indices and packing of the molecules on (010), (001) and (100) faces, (a) **4-FBO**, (b) **4-CBO** (c) **4-BBO** (d) **4-IBO**

**NOTE:** Structure graphics shown in the figures were created using the X-Seed software package version 4.0[3]

**6. (a) Energy calculations:**

Crystal Explorer 21.5[4] was used for the calculation of interaction energy and the generation of energy framework diagrams of the single crystals of 4-FBO, 4-CBO, 4-BBO and 4-IBO based on their crystal structure. The energy scale factor is 70 and the energy threshold is 2 kJ $mol^{-1}$.The interaction energy is estimated from the accurate unperturbed method CE-B3LYP/6-31g (d,p) energy model for **4-FBO, 4-CBO** and **4-BBO**. And for **4-IBO** energy is calculated by fast unperturbed molecular wave function using the CE-HF/3-21G energy model.

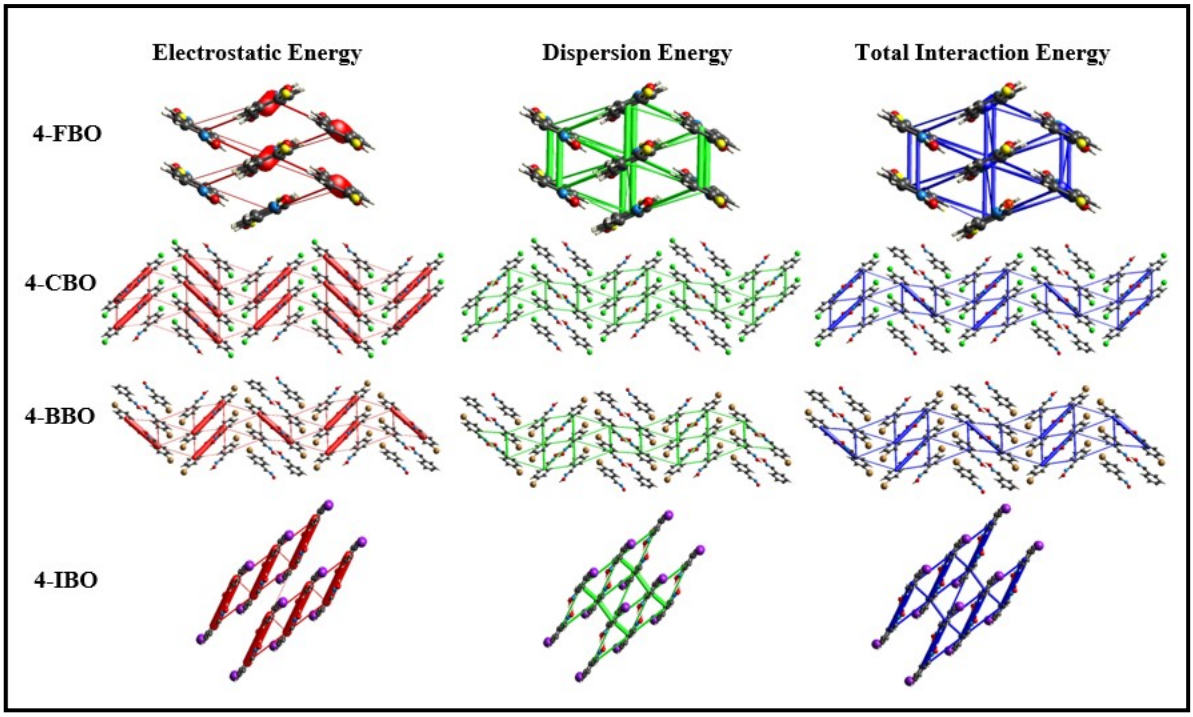
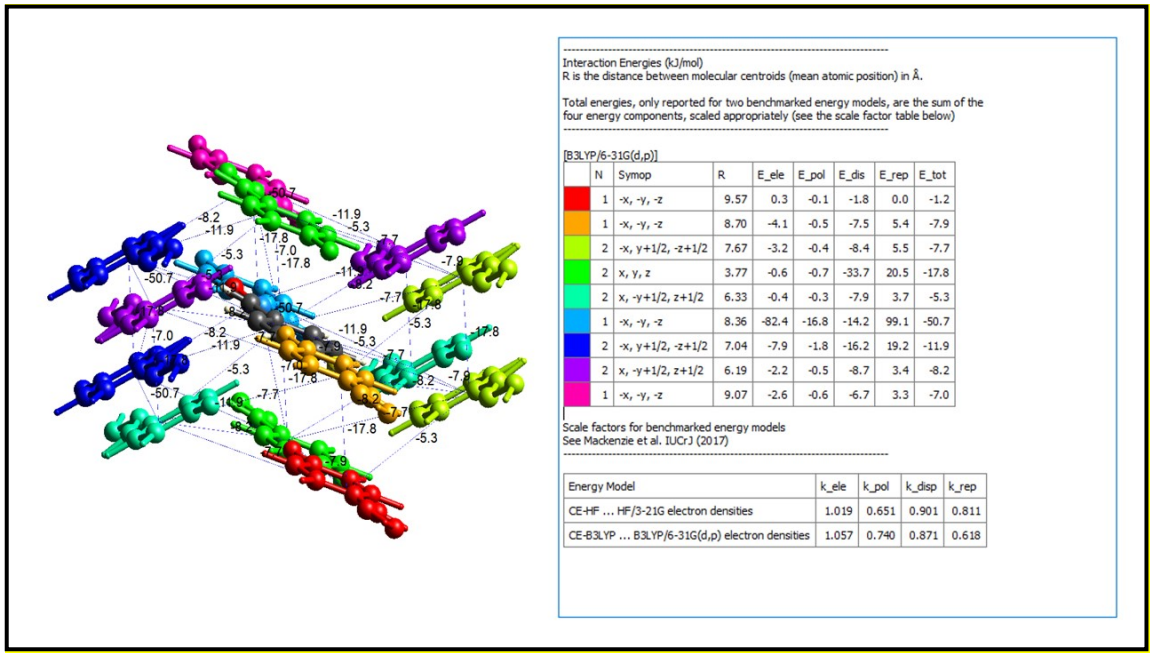



**Figure S7:** Energy frameworks corresponding to the different energy components in **4-FBO** (Brittle), **4-CBO** (plastic), **4-BBO** (elastic) and **4-IBO (**plastic). The energy scale factor is 70 and the energy threshold is 2 kJ $mol^{-1}$.

**(b) Quantitative parameters of different energies contributing to intermolecular interactions:**



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

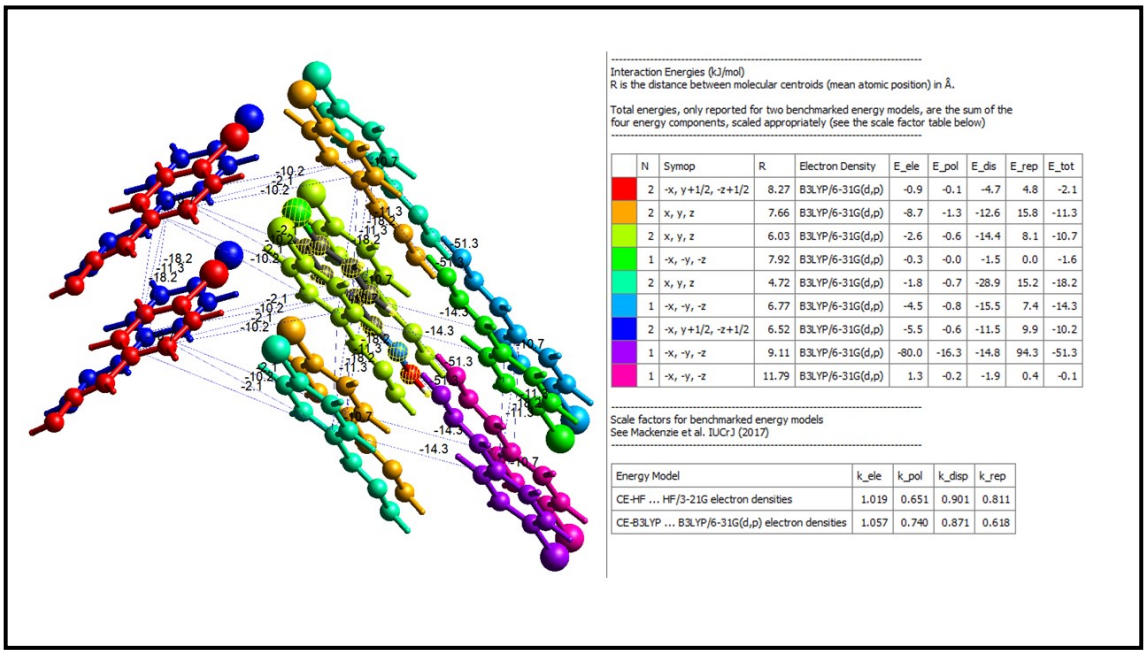
[B3LYP/6-31G(d,p)]

| | N | Symop | R | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|---|---|---|---|---|---|---|---|
| | 1 | -x, -y, -z | 9.57 | 0.3 | -0.1 | -1.8 | 0.0 | -1.2 |
| | 1 | -x, -y, -z | 8.70 | -4.1 | -0.5 | -7.5 | 5.4 | -7.9 |
| | 2 | -x, y+1/2, -z+1/2 | 7.67 | -3.2 | -0.4 | -8.4 | 5.5 | -7.7 |
| | 2 | x, y, z | 3.77 | -0.6 | -0.7 | -33.7 | 20.5 | -17.8 |
| | 2 | x, -y+1/2, z+1/2 | 6.33 | -0.4 | -0.3 | -7.9 | 3.7 | -5.3 |
| | 1 | -x, -y, -z | 8.36 | -82.4 | -16.8 | -14.2 | 99.1 | -50.7 |
| | 2 | -x, y+1/2, -z+1/2 | 7.04 | -7.9 | -1.8 | -16.2 | 19.2 | -11.9 |
| | 2 | x, -y+1/2, z+1/2 | 6.19 | -2.2 | -0.5 | -8.7 | 3.4 | -8.2 |
| | 1 | -x, -y, -z | 9.07 | -2.6 | -0.6 | -6.7 | 3.3 | -7.0 |

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_disp | k_rep |
|---|---|---|---|---|
| CE-HF ... HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| CE-B3LYP ... B3LYP/6-31G(d,p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

**Fig. S8** Energy framework diagram of total energy (annotated) and energy calculation table of **4-FBO**.



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

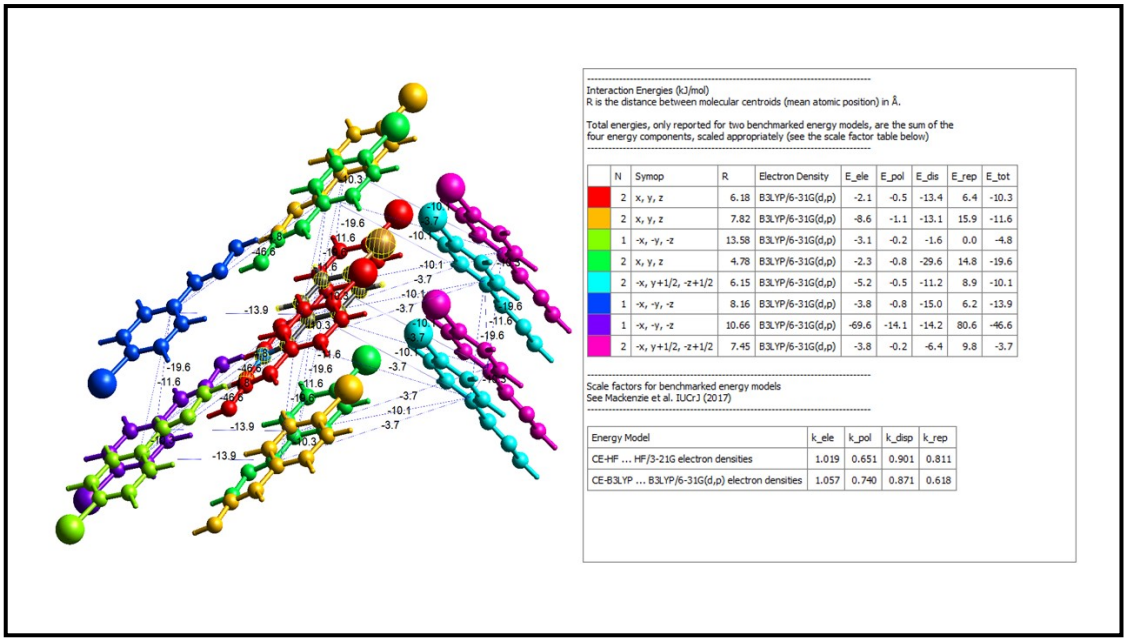
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | -x, y+1/2, -z+1/2 | 8.27 | B3LYP/6-31G(d,p) | -0.9 | -0.1 | -4.7 | 4.8 | -2.1 |
| | 2 | x, y, z | 7.66 | B3LYP/6-31G(d,p) | -8.7 | -1.3 | -12.6 | 15.8 | -11.3 |
| | 2 | x, y, z | 6.03 | B3LYP/6-31G(d,p) | -2.6 | -0.6 | -14.4 | 8.1 | -10.7 |
| | 1 | -x, -y, -z | 7.92 | B3LYP/6-31G(d,p) | -0.3 | -0.0 | -1.5 | 0.0 | -1.6 |
| | 2 | x, y, z | 4.72 | B3LYP/6-31G(d,p) | -1.8 | -0.7 | -28.9 | 15.2 | -18.2 |
| | 1 | -x, -y, -z | 6.77 | B3LYP/6-31G(d,p) | -4.5 | -0.8 | -15.5 | 7.4 | -14.3 |
| | 2 | -x, y+1/2, -z+1/2 | 6.52 | B3LYP/6-31G(d,p) | -5.5 | -0.6 | -11.5 | 9.9 | -10.2 |
| | 1 | -x, -y, -z | 9.11 | B3LYP/6-31G(d,p) | -80.0 | -16.3 | -14.8 | 94.3 | -51.3 |
| | 1 | -x, -y, -z | 11.79 | B3LYP/6-31G(d,p) | 1.3 | -0.2 | -1.9 | 0.4 | -0.1 |

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_disp | k_rep |
|---|---|---|---|---|
| CE-HF ... HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| CE-B3LYP ... B3LYP/6-31G(d,p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

**Fig. S9** Energy framework diagram of total energy (annotated) and energy calculation table of **4-CBO**



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

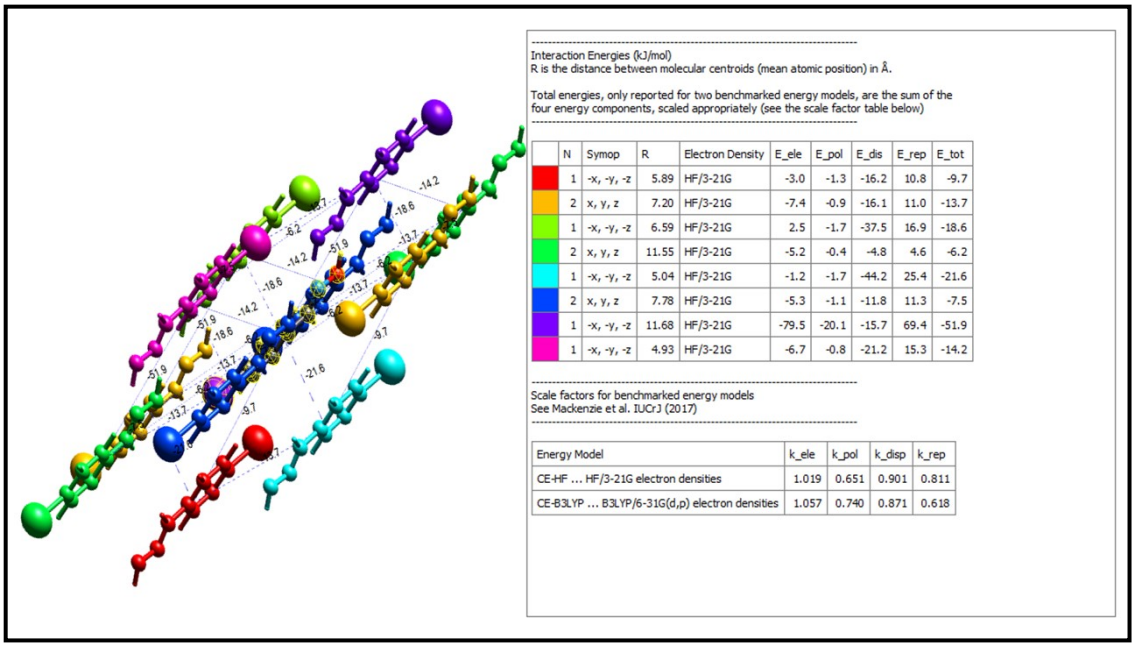
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | x, y, z | 6.18 | B3LYP/6-31G(d,p) | -2.1 | -0.5 | -13.4 | 6.4 | -10.3 |
| | 2 | x, y, z | 7.82 | B3LYP/6-31G(d,p) | -8.6 | -1.1 | -13.1 | 15.9 | -11.6 |
| | 1 | -x, -y, -z | 13.58 | B3LYP/6-31G(d,p) | -3.1 | -0.2 | -1.6 | 0.0 | -4.8 |
| | 2 | x, y, z | 4.78 | B3LYP/6-31G(d,p) | -2.3 | -0.8 | -29.6 | 14.8 | -19.6 |
| | 2 | -x, y+1/2, -z+1/2 | 6.15 | B3LYP/6-31G(d,p) | -5.2 | -0.5 | -11.2 | 8.9 | -10.1 |
| | 1 | -x, -y, -z | 8.16 | B3LYP/6-31G(d,p) | -3.8 | -0.8 | -15.0 | 6.2 | -13.9 |
| | 1 | -x, -y, -z | 10.66 | B3LYP/6-31G(d,p) | -69.6 | -14.1 | -14.2 | 80.6 | -46.6 |
| | 2 | -x, y+1/2, -z+1/2 | 7.45 | B3LYP/6-31G(d,p) | -3.8 | -0.2 | -6.4 | 9.8 | -3.7 |

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_disp | k_rep |
|---|---|---|---|---|
| CE-HF ... HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| CE-B3LYP ... B3LYP/6-31G(d,p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

**Fig. S10** Energy framework diagram of total energy (annotated) and energy calculation table of **4-BBO**



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | -x, -y, -z | 5.89 | HF/3-21G | -3.0 | -1.3 | -16.2 | 10.8 | -9.7 |
| | 2 | x, y, z | 7.20 | HF/3-21G | -7.4 | -0.9 | -16.1 | 11.0 | -13.7 |
| | 1 | -x, -y, -z | 6.59 | HF/3-21G | 2.5 | -1.7 | -37.5 | 16.9 | -18.6 |
| | 2 | x, y, z | 11.55 | HF/3-21G | -5.2 | -0.4 | -4.8 | 4.6 | -6.2 |
| | 1 | -x, -y, -z | 5.04 | HF/3-21G | -1.2 | -1.7 | -44.2 | 25.4 | -21.6 |
| | 2 | x, y, z | 7.78 | HF/3-21G | -5.3 | -1.1 | -11.8 | 11.3 | -7.5 |
| | 1 | -x, -y, -z | 11.68 | HF/3-21G | -79.5 | -20.1 | -15.7 | 69.4 | -51.9 |
| | 1 | -x, -y, -z | 4.93 | HF/3-21G | -6.7 | -0.8 | -21.2 | 15.3 | -14.2 |

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

| Energy Model | k_ele | k_pol | k_disp | k_rep |
|---|---|---|---|---|
| CE-HF ... HF/3-21G electron densities | 1.019 | 0.651 | 0.901 | 0.811 |
| CE-B3LYP ... B3LYP/6-31G(d,p) electron densities | 1.057 | 0.740 | 0.871 | 0.618 |

**Fig. S11** Energy framework diagram of total energy (annotated) and energy calculation table of **4-IBO**

**Note:** All these energy calculations have been done in crystal explorer 21.5 software[4]

## 7. Crystallographic information:

Although the crystal structures of all the compounds in this study were reported before in the literature,[5-8] unit cell parameters of all these crystals were determined to confirm the structures.

**Table S5**: Unit cell parameters of para-substituted benzaldehyde oximes:

| **Cell parameters** | **4-FBO** | **4-CBO** | **4-BBO** | **4-IBO** |
|---|---|---|---|---|
| Formula | $C_7 H_6 F N O$ | $C_7 H_6 Cl N O$ | $C_7 H_6 Br N O$ | $C_7 H_6 I N O$ |
| Molecular weight (g $mol^{-1}$) | 139.13 | 155.58 | 200.03 | 247.03 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $P\,2_1/c$ | $P\,2_1/c$ | $P\,2_1/c$ | $P$-1 |
| a (Å) | 14.213(4) | 6.086(2) | 6.161(4) | 7.203(4) |
| b (Å) | 3.767(9) | 4.754(2) | 4.766(4) | 7.394(4) |
| c (Å) | 11.936(4) | 25.153(8) | 25.187(3) | 7.781(3) |
| α (°) | 90 | 90 | 90 | 107.83(2) |
| β (°) | 99.21(2) | 93.70(3) | 94.00(2) | 100.82(2) |
| γ (°) | 90 | 90 | 90 | 90.77(2) |
| V ($Å^3$) | 630.905 | 726.231 | 737.773 | 386.482 |
| Reported Refcode | JIYYIC[5] | CBALOS02[6] | BAGWOW01[7] | GIKSOK[8] |

**Note:** Unit cell parameters of the crystal structure of the compounds were compared with previously reported structures.[5-8]

## 8. H-bonding parameters:

**Table S6**: H-bonding parameters of para-substituted benzaldehyde oximes:

| **Name of the compound** | **H-Bonds** | **D H (Å)** | **H···A (Å)** | **D···A (Å)** | **∠D H···A (°)** |
|---|---|---|---|---|---|
| 4-FBO | O(1) H(6)···N(1) | 1.00(2) | 1.88(2) | 2.799(1) | 151.8(1) |
| | C(7) H(5)···O(1) | 0.95 | 2.498 | 3.423(1) | 165 |
| | C(5) H(3)···F(1) | 0.949 | 2.646 | 3.442(1) | 141.57 |
| | *C(5) H(3)···π | 0.949 | 3.308 | 3.932 | 125.12 |
| 4-CBO | O(1) H(1)···N(1) | 0.92(3) | 1.952(2) | 2.824(2) | 155.56(2) |
| | C(3) H(2)···O(1) | 0.96(2) | 2.58(2) | 3.442(2) | 150.09(2) |
| | **C(6) H(6)··· π | 0.95(2) | 2.975(2) | 3.855(2) | 156.03(1) |
| 4-BBO | O(1) H(1)···N(1) | 0.91 | 1.94 | 2.820(5) | 162 |
| | C(5) H(4)···O(1) | 0.95 | 2.621 | 3.510(4) | 155.7 |
| 4-IBO | O(1) H(6)···N(1) | 0.807(3) | 2.08(3) | 2.839(2) | 156(3) |

* In case of **4-FBO,** C(5) H(3)···π interactions are calculated by considering the centroid of C(2) and C(3) of one molecule and C(5) H(3) of other molecule in the crystal structure.

** In case of **4-CBO,** C(6) H(6)··· π interactions are calculated by considering the C(6) of one molecule as π centre and C(6) H(6) of other molecule in the crystal structure.

**9. Description of Animations:**

The mechanical behaviour of all the crystals was recorded by videography to show real-time mechanical properties. Video S1 shows the brittle nature of **4-FBO**, Video S2 shows the plastic behaviour of **4-CBO**, Video S3 shows the elastic behaviour of **4-BBO** and Video S4 shows the plastic nature of **4-IBO**.

**10. References**


1. Q. Feng, H. Huang, and J. Sun *Org. Lett.* 2021, **23**, 2431−2436
2. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, J. Appl. Cryst. 2020, **53**, 226-235
3. L. J. Barbour,X-Seed. *J. Supramol. Chem.,*2001, **1**, 189.
4. D. Jayatilaka, and M. A. Spackman, *J. Appl. Cryst*., 2021, **54**,1006-1011.
5. L. R. Gomes, J. N. Low, T.V. Mourik, H Früchtl, M. V.N. de Souza, C. F. da Costa and J. L. Wardell, *Z. Naturforsch.* 2019; **74**, 319–334
6. J.T. Mague, Y. E. Bakri*, CSD Communication*, 2016
7. L. Zhang, H. Chen, Z. Zha and Z. Wang, *Chem. Commun.,* 2012, **48**, 6574–6576
8. C.B. Aakeröy, A. S. Sinha, K. N. Epa, P. D. Chopade, M. M. Smith and J. Desper, *Cryst. Growth Des.,* 2013, **13**, 2687–2695