Experimental and theoretical analysis of *lp…π* intermolecular interactions in derivatives of 1,2,4-triazoles

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Supporting Information

Section-1

Table-S1: IUPAC name of the synthesized compounds along with their code.

-X	IUPAC Name	Code
-F	(E)-3-(4-fluoro-3-phenoxyphenyl)-4-((4-fluorobenzylidene)amino)-1H-1,2,4-triazole-5(4H)-thione	**TRZ-1**
-Cl	(E)-4-((4-chlorobenzylidene)amino)-3-(4-fluoro-3-phenoxyphenyl)-1H-1,2,4-triazole-5(4H)-thione	**TRZ-2**

Table S2: Characterization of the Synthesized Compounds

Compound Code	Molecular Formula	Yield (%)	Melting Point (Onset Value from DSC Plot)
TRZ-1	$C_{26}H_{23}N_5O_2F_2S_1$	68	163.2ºC
TRZ-2	$C2_6H_{23}N_5O_2F_1Cl_1S_1$	73	146.3ºC

IR Characterization

Figure S1: IR Data for all the compounds recorded using KBr Plates: All NMR experiments were recorded on 400MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

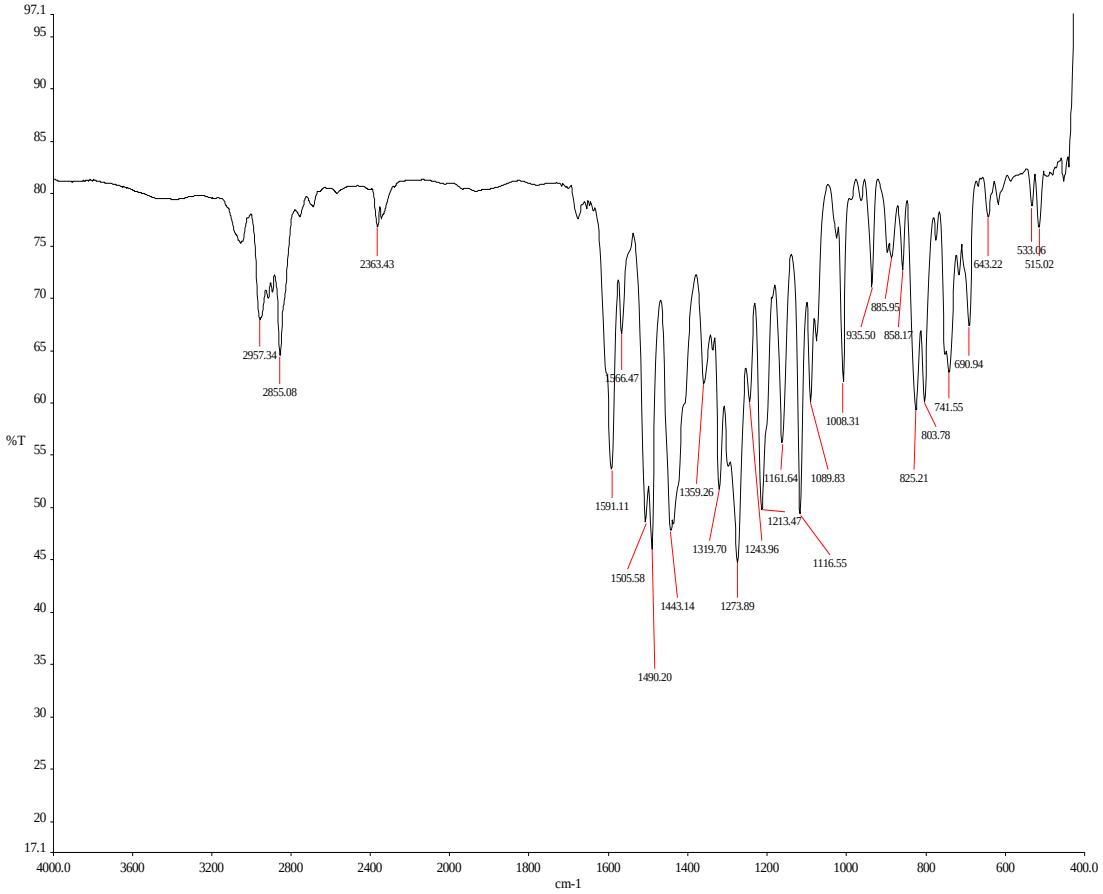


Figure-S1 (a) IR spectral data of **TRZ-1.**

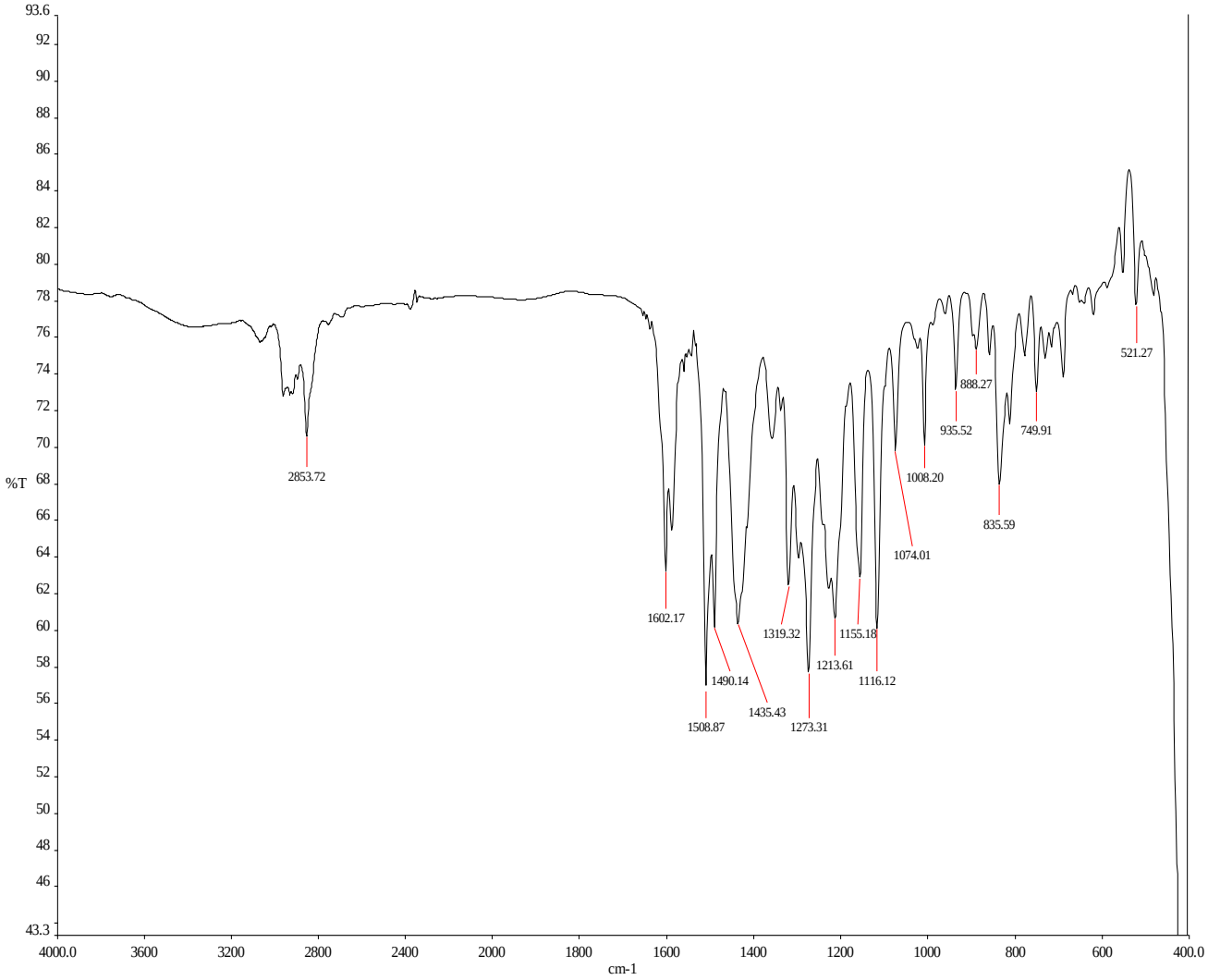


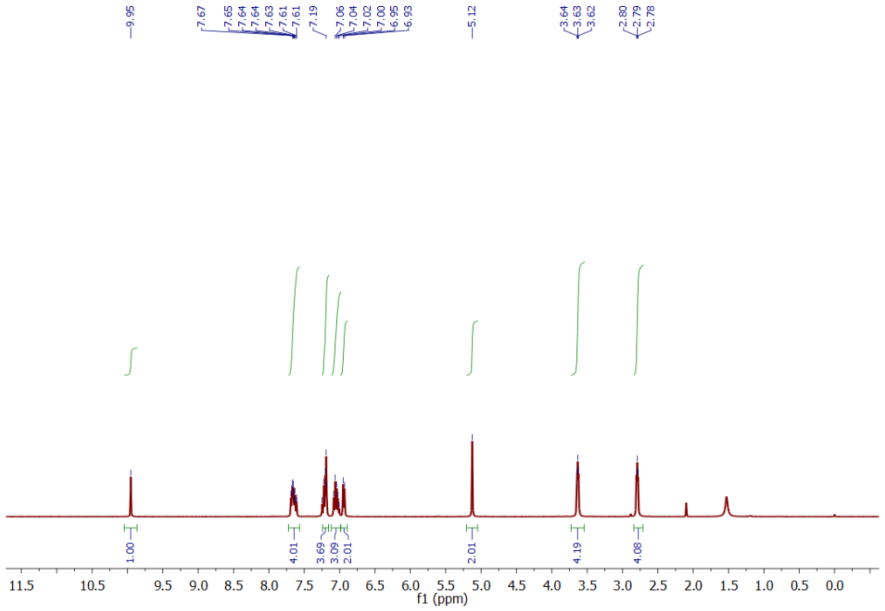
Figure-S1 (b) IR spectral data of **TRZ-2**.

NMR Characterization

Figure S2: All NMR experiments were recorded on 400MHz spectrometer (from Bruker) in $CDCl_3$ as solvent.

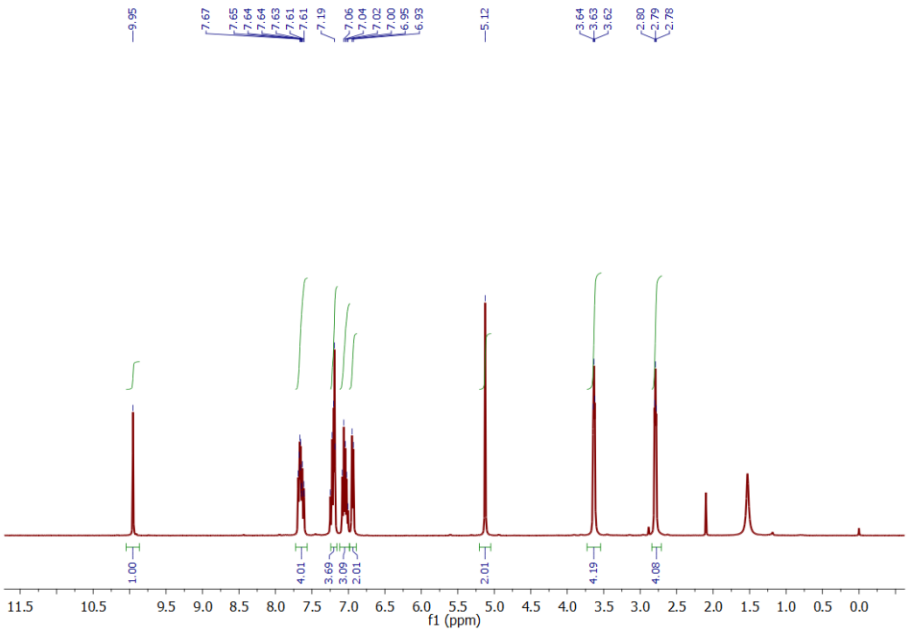
(a) TRZ-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.98 – 7.47 (m, 4H), 7.26 – 7.16 (m, 3H), 7.11 – 6.99 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 2H), 5.12 (s, 2H), 3.95 – 3.38 (t, 4H), 3.16 – 2.53 (t, 4H).



(b) TRZ-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.77 – 7.48 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.12 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 5.08 (s, 2H), 3.61 – 3.56 (t, 4H), 2.89 – 2.52 (t, 4H).



DSC Analysis

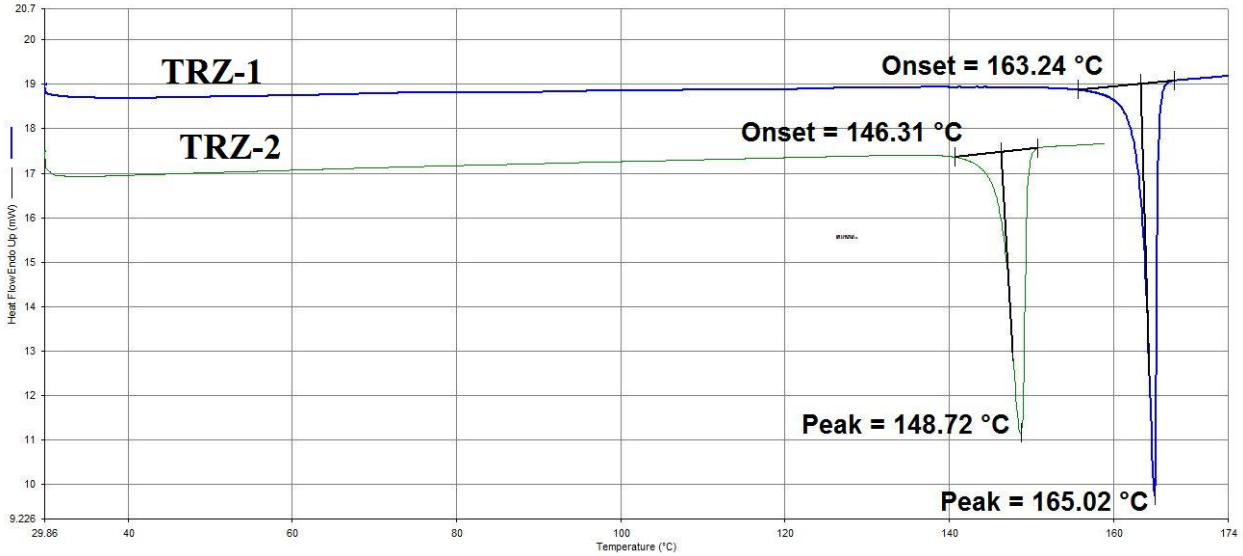


Figure –S3(a): DSC traces of the synthesised compounds (@ 5˚C/min).

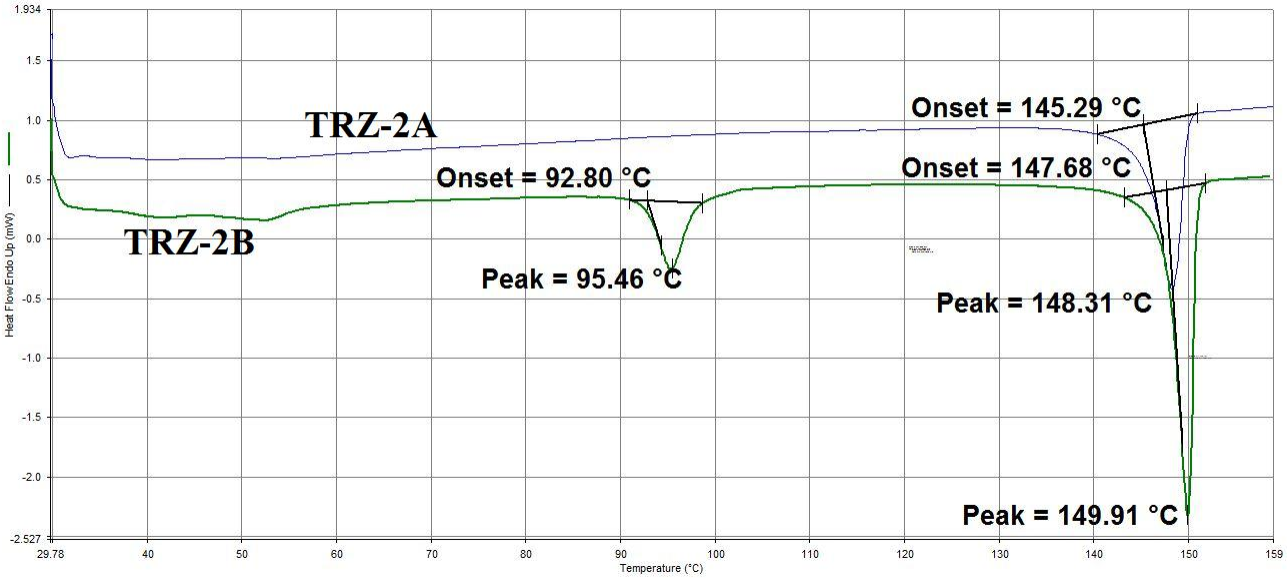


Figure –S3(b): DSC traces of the crystals of **TRZ-2A** and **TRZ-2B** (@ 5˚C/min).

TG Analysis

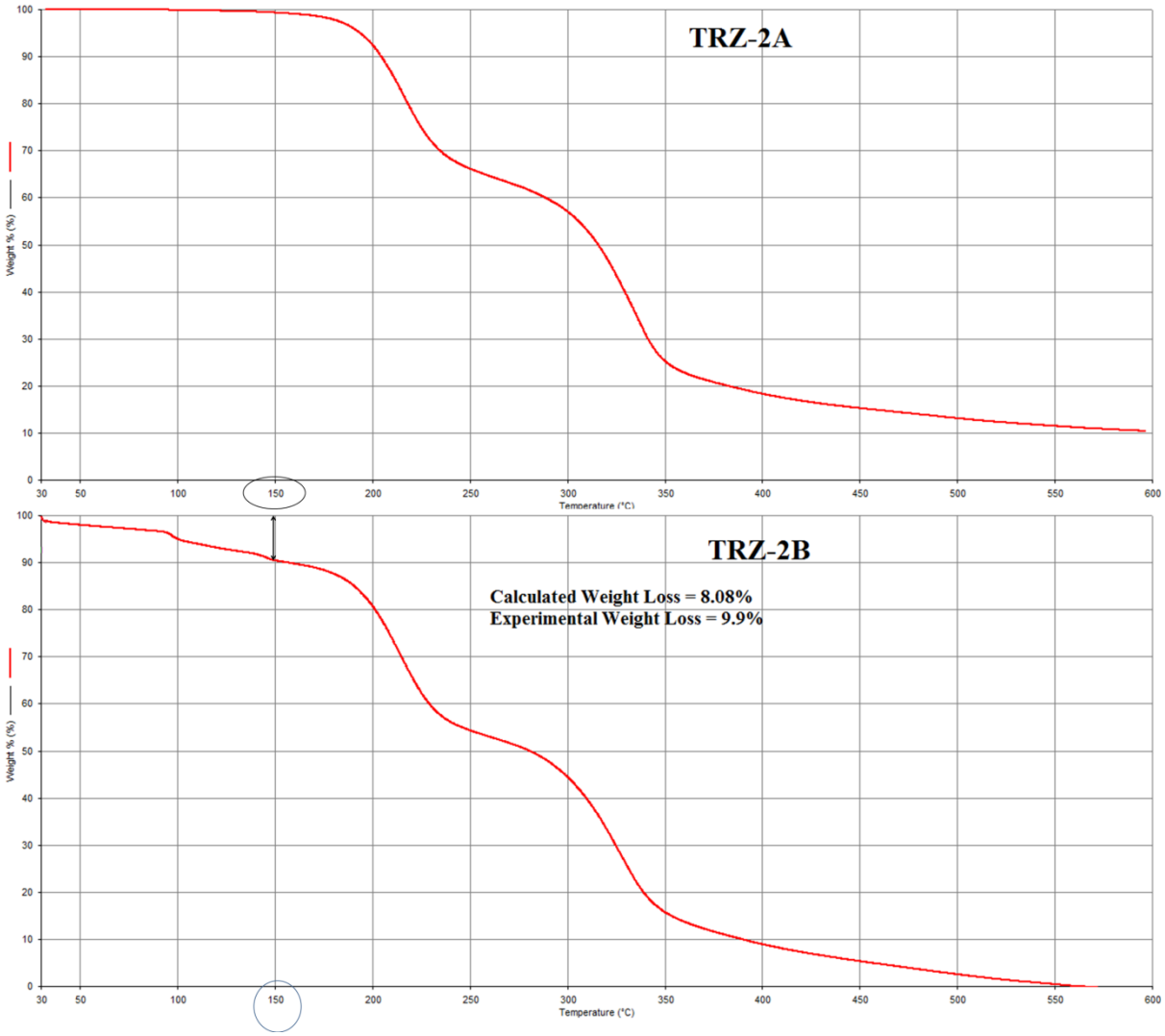


Figure-S4: TG analysis depicting different % of weight loss till the melting point of 150 °C for crystals of **TRZ-2A**(above) and **TRZ-2B**(below).

Hot Stage Microscopy

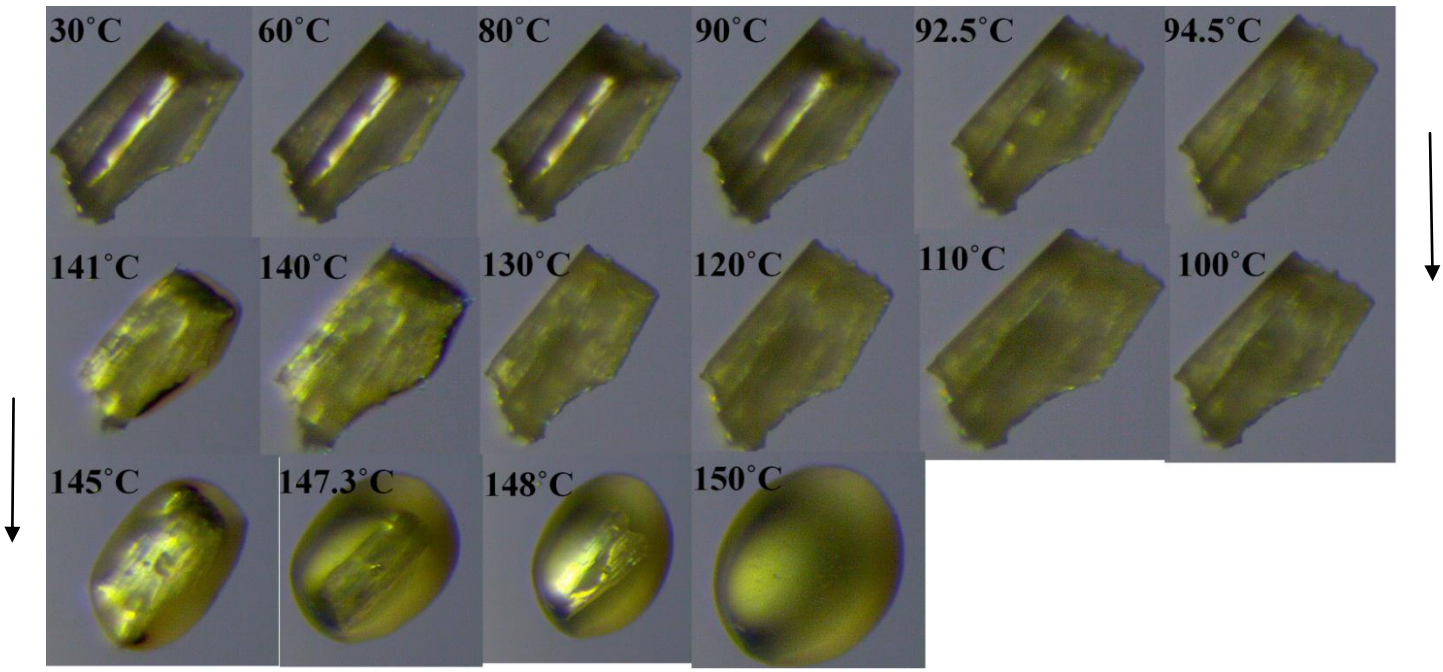


Figure-S5: Optical images of a crystal of **TRZ-2B** obtained on heating, taken as a function of change in temperature.

Powder Diffraction

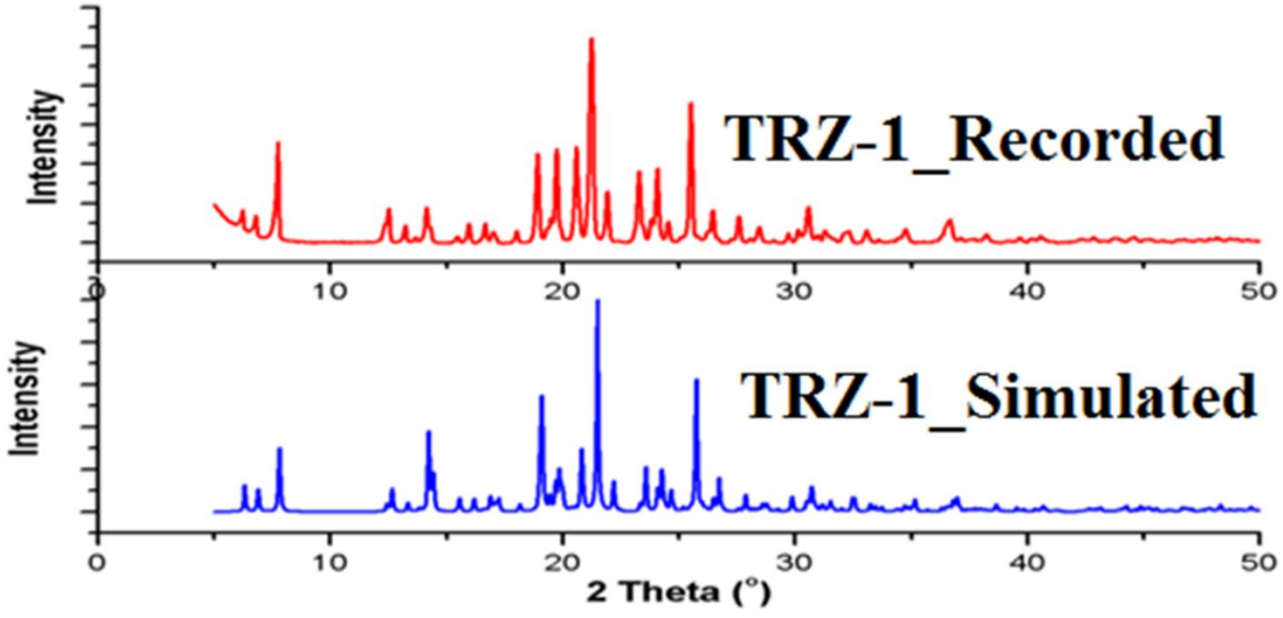


Figure-S6(a): Experimental and simulated powder diffraction pattern for **TRZ-1.**

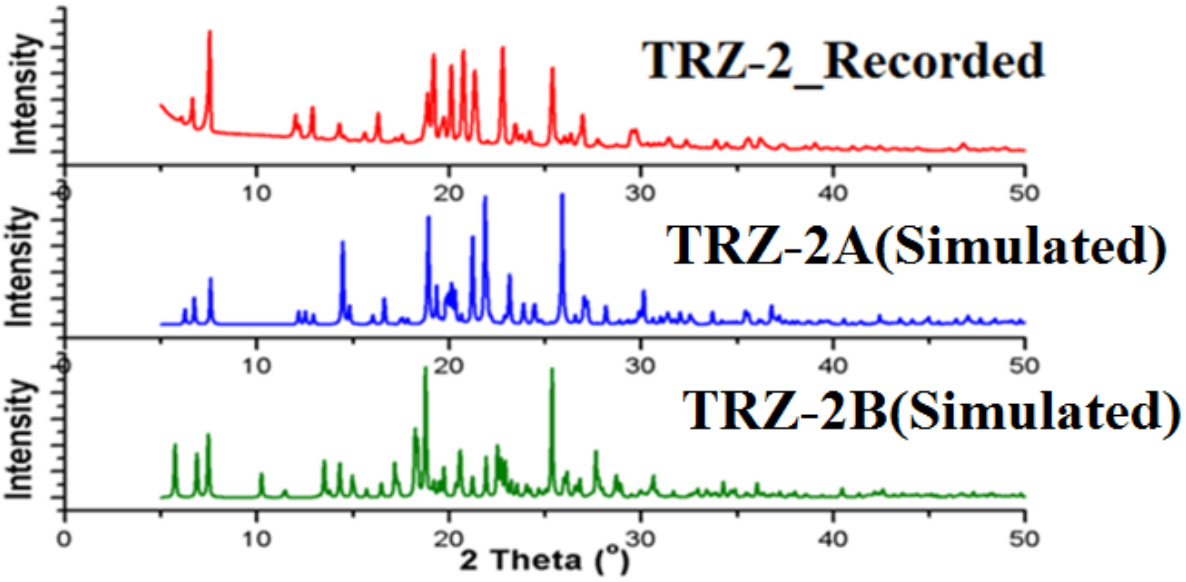


Figure-S6(b): Experimental and simulated powder diffraction pattern for **TRZ-2A** and **TRZ-2B.**

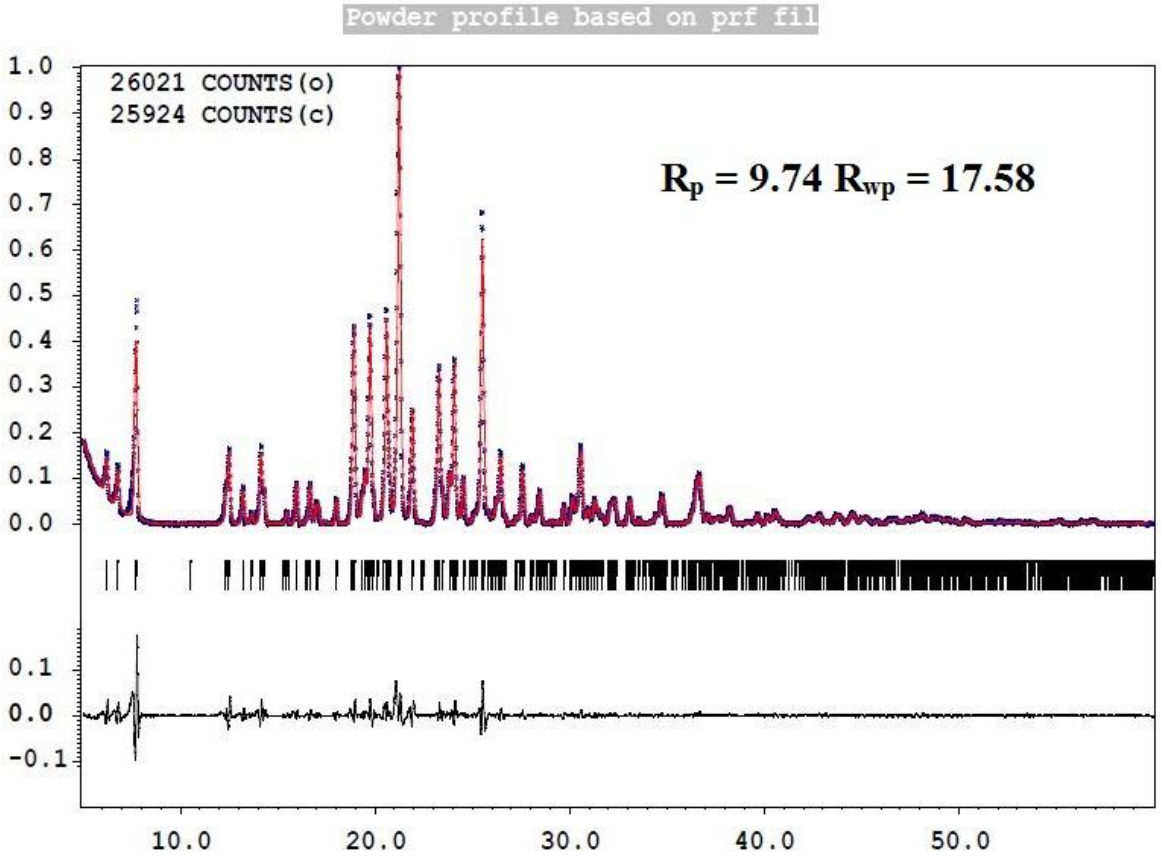


Figure-S6(c): Powder profile fitting of **TRZ-1**.

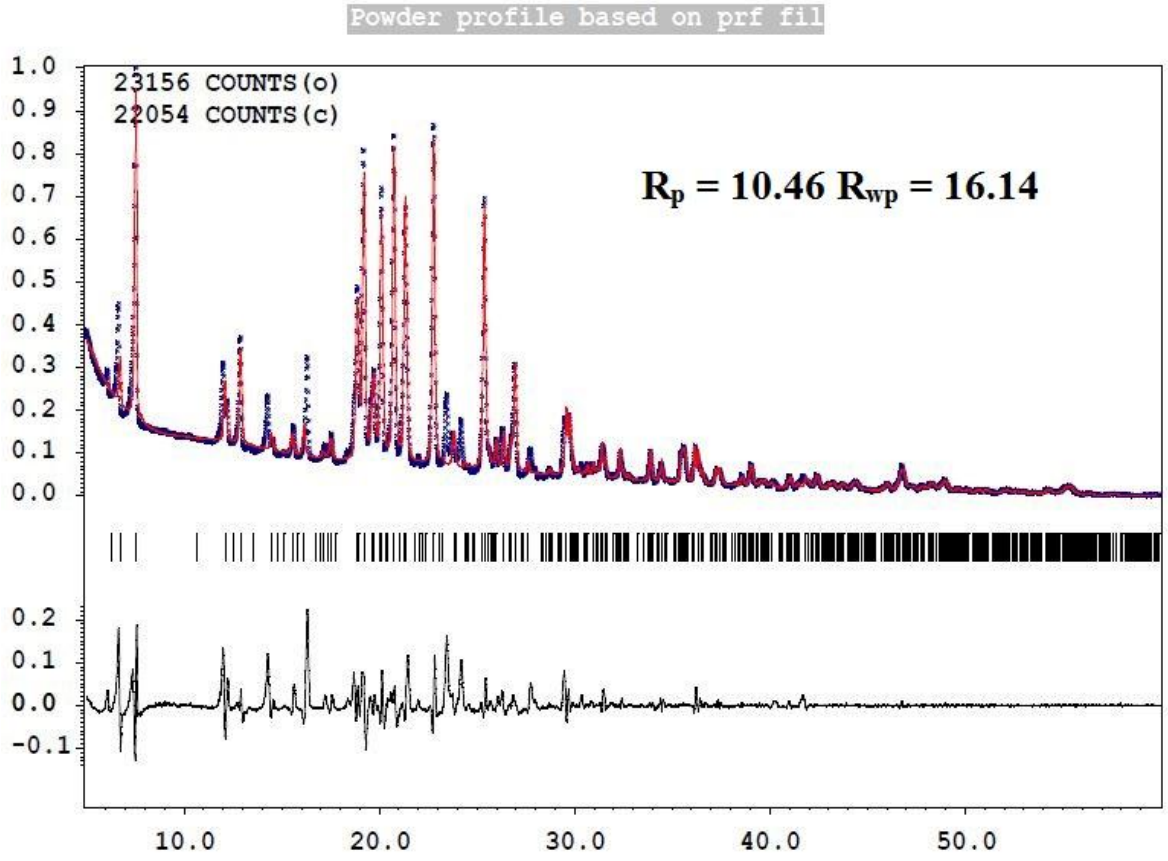


Figure-S6(d): Powder profile fitting of **TRZ-2**.

Table-S3: Crystallographic and refinement Data

DATA	**TRZ-1**	**TRZ-2A**	**TRZ-2B**
Formula	$C_{26}H_{23}N_5F_2O_2S_1$	$C_{26}H_{23}F_1N_5O_2Cl_1S_1$	$C_{26}H_{23}N_5F_1O_2S_1Cl_1$, 0.5($C_7H_8$)
CCDC Number	963711	963712	963713
Formula Weight	507.55	524	570.07
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	*P*-1	*P*-1	*P*-1
Wavelength (Å)	0.71073	0.71073	0.71073
a(Å)	6.3326(3)	6.2030(5)	6.5674(8)
b(Å)	13.4313(8)	13.8341(12)	13.5041(17)
c(Å)	14.9364(8)	15.1090(14)	16.236(2)
α(°)	72.429(2)	71.303(4)	71.902(6)
β(°)	79.140(2)	80.718(4)	86.120(6)
γ(°)	89.112(2)	88.344(4)	89.592(6)
Volume($Å^3$)	1188.29(11)	1211.68(18)	1365.4(3)
Z	2	2	2
Density(g cm^{-3})	1.419	1.436	1.370
μ(mm^{-1})	0.187	0.287	0.260
F(000)	528	544	590

θ (min ,max)	2.46, 25.00	1.44, 25.00	1.72, 25.00
Treatment of Hydrogens	Fixed	Fixed	Fixed
$h_{mim,max}$, $k_{min,max}$, $l_{min,max}$	(-7,7), (-15,15), (-17,17)	(-7,7), (-16,15), (-17,17)	(-7,7), (-16,16), (-20,20)
No. of reflections	20226	18352	16778
No. of unique ref./obs. Ref	4110, 3564	4264, 3955	4784, 4375
R_{obs}, R_{all}	0.0636, 0.0748	0.0347, 0.0369	0.0427, 0.0462
$wR_{2\ (obs)}$, $wR_{2\ (all)}$	0.1325, 0.1383	0.0936, 0.0958	0.1108, 0.1135
$\Delta\rho_{min\ ,max}$ (e $Å^{-3}$)	-0.251, 0.375	-0.377, 0.230	-0.777, 0.413
G. o. F	1.149	1.048	1.046

Torsion Angle

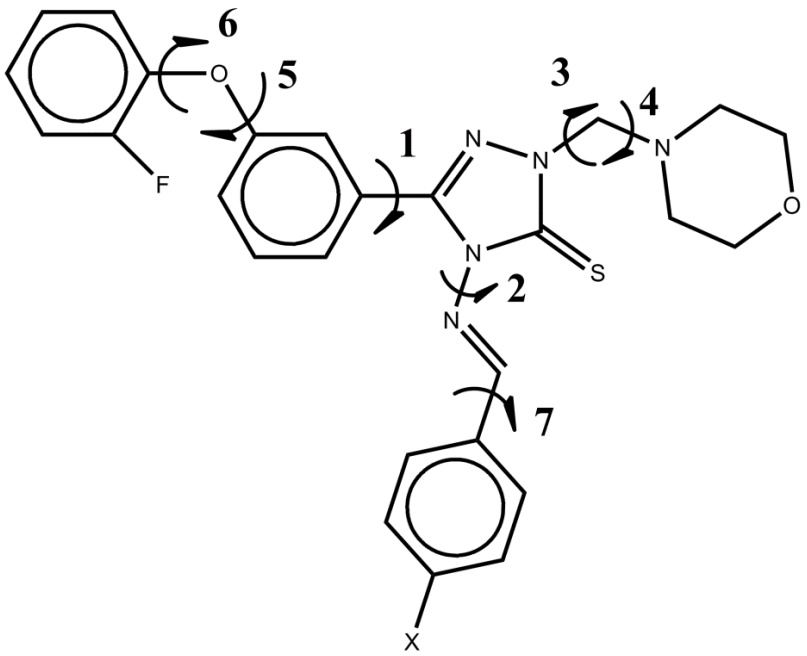


Table-S4: List of important torsion angles (°) for **TRZ-1, TRZ-2A** and **TRZ-2B** and molecules retrieved from the CSD search at the crystal geometry and the gas phase geometry (in italics)

Crystal Code	Torsion-1	Torsion-2	Torsion-3	Torsion-4	Torsion-5	Torsion-6	Torsion-7
TRZ-1	165.5(3) *152.5*	164.2(3) *168.5*	105.8(3) *102*	72.2(3) *68.8*	96.0(3) *76.1*	165.6(3) *171.7*	175.1(3) *177.7*
TRZ-2A	165.3(3) *151.5*	163.9(3) *171.4*	109.2(2) *102.1*	72.8(3) *68.9*	85.6(3) *78.0*	167.3(3) *173.4*	176.1(3) *177.6*
TRZ-2B	161.3(3) *151.2*	165.5(3) *172.5*	100.0(2) *102.1*	72.7(2) *68.8*	96.0(2) *86.7*	175.8(3) *180*	175.5(3) *178.1*

AZUTAR	157.7(1) *151.6*	150.6(1) *153.0*	-	-	-	-	177.3(1) *179.2*
AZUTEV	152.0(1) *146.1*	176.2(1) *177.8*	-	-	-	-	170.5(1) *175.6*
EXITUB	157.1(3) *154.0*	142.3(3) *157.4*	-	-	-	-	166.2(3) *175.5*
ULIBAT	150.7(2) *149.3*	154.9(1) *154.9*	-	-	-	-	179.3(1) *178.8*

Section 3: Lattice Energy Calculations

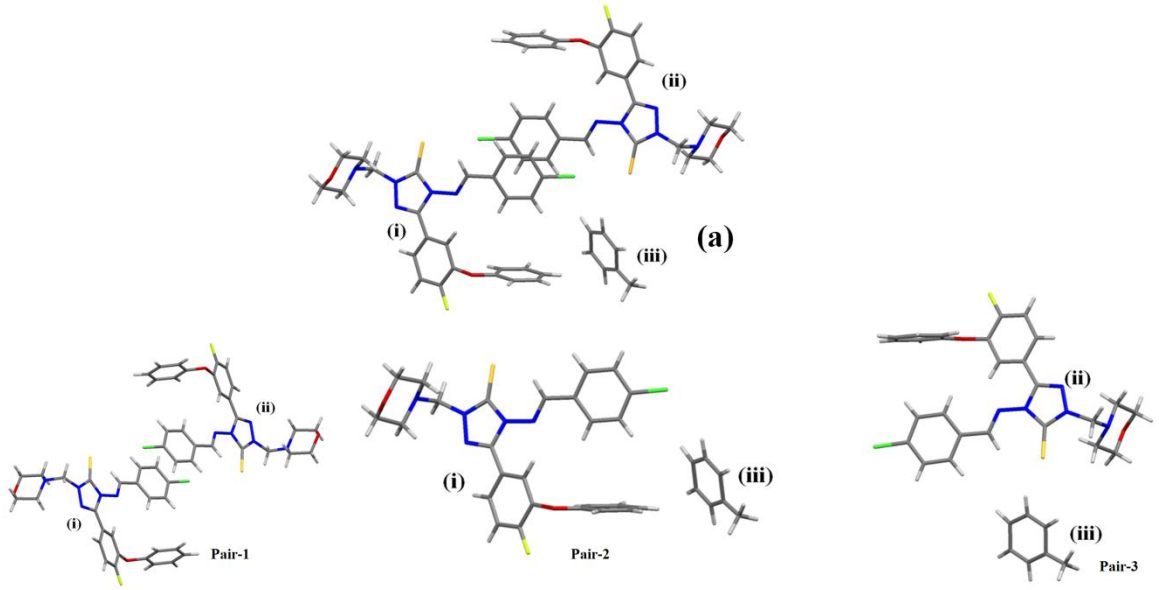
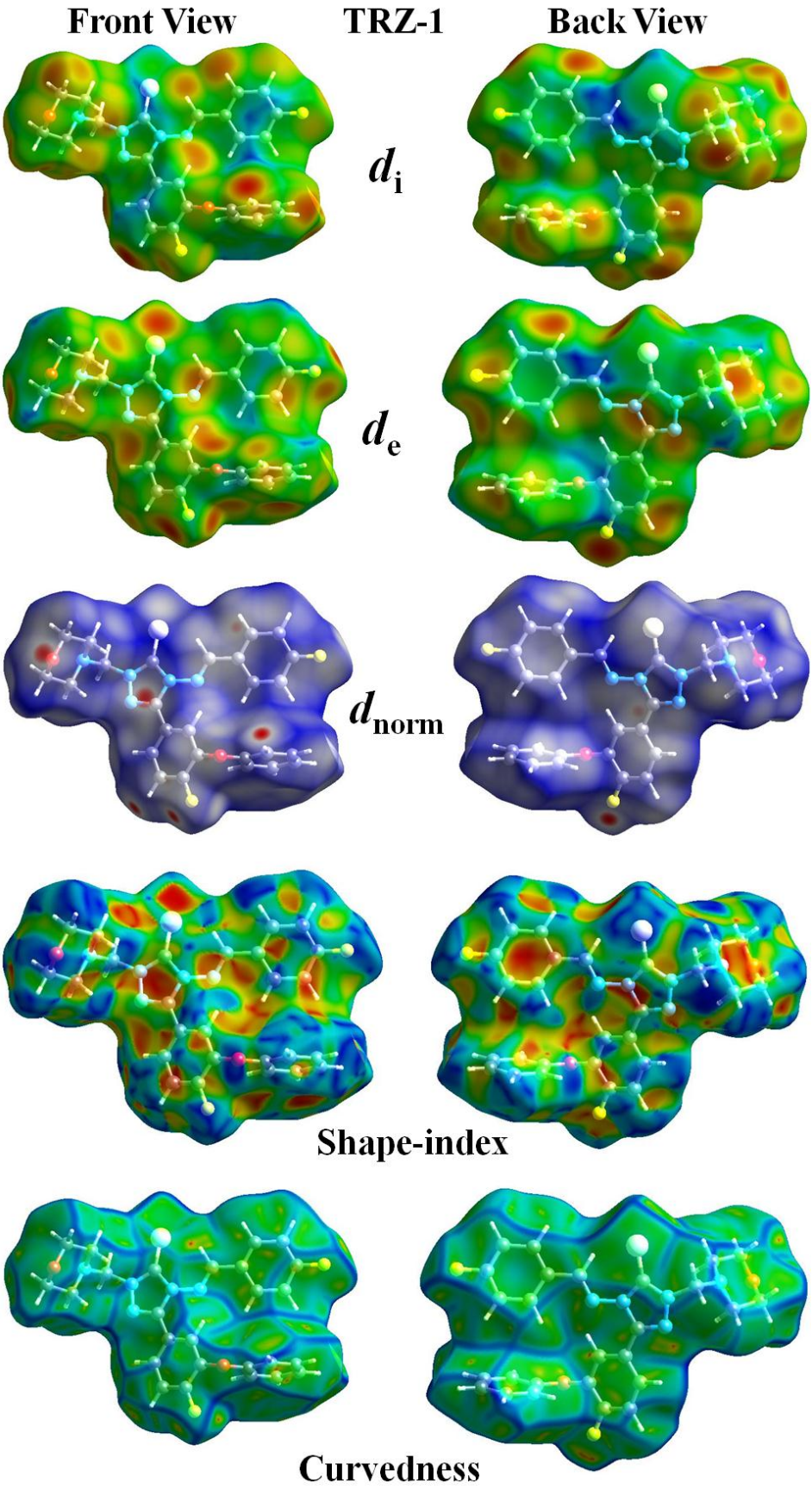
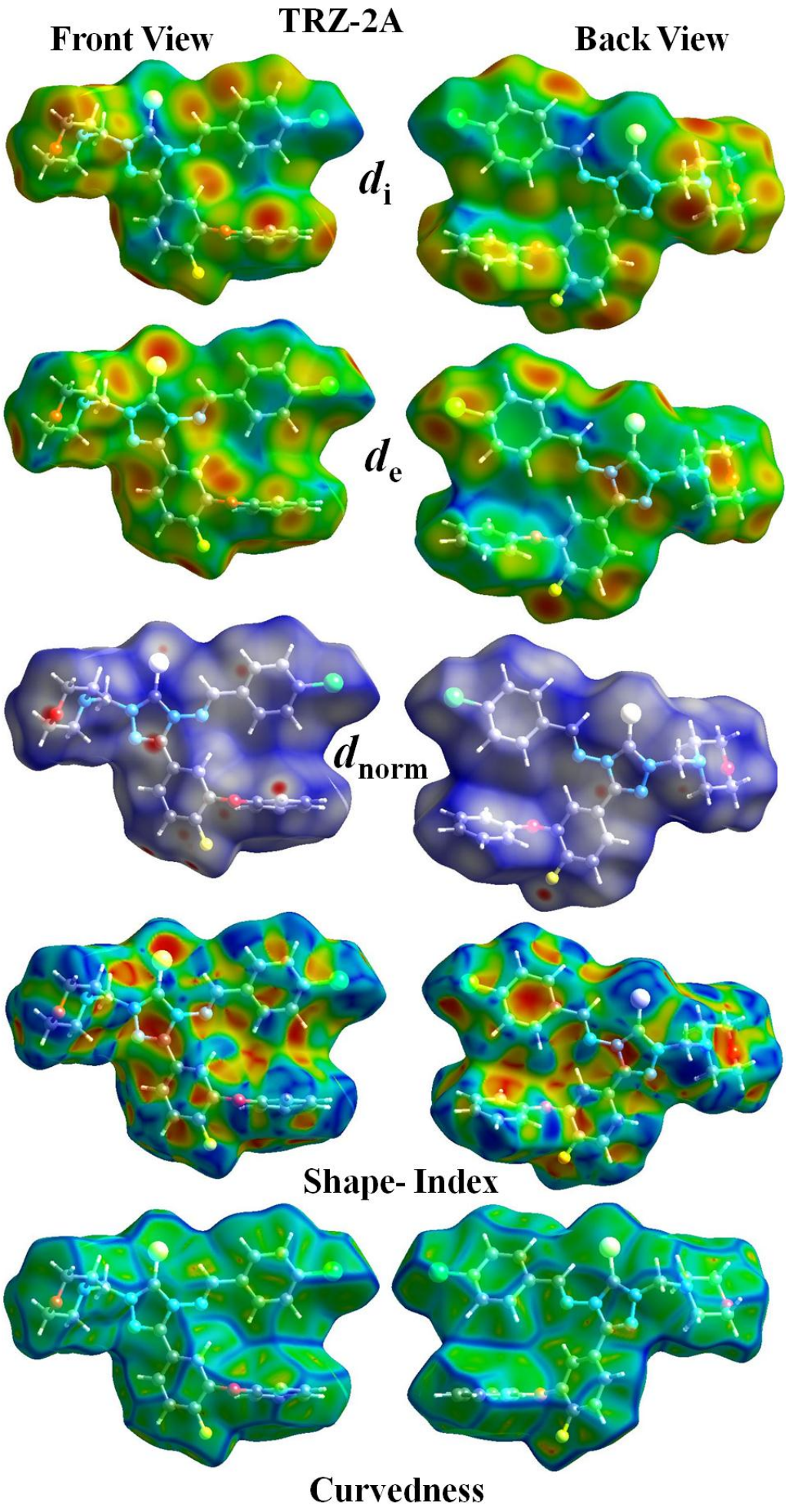


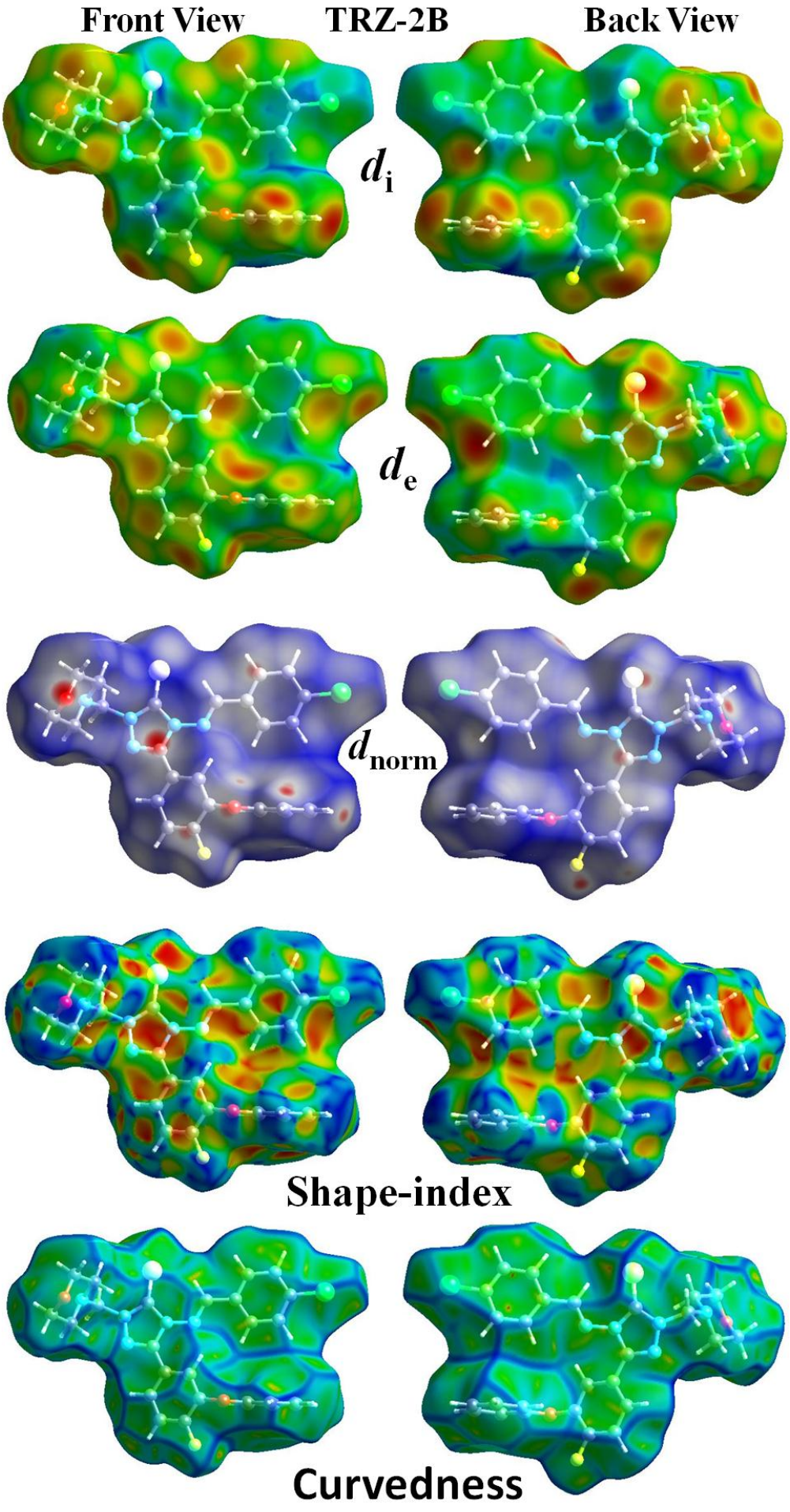
Figure-S7:(a) Represents the asymmetric unit of **TRZ-2B** after reducing its symmetry from P-1 to P1. Pair-1 represents the molecule (i) and (ii) taken for the lattice energy calculation. Pair-2 represents the molecule (i) and (iii) taken for the lattice energy calculation. Pair-3 represents the molecule (ii) and (iii) taken for the lattice energy calculation.

Section 4: Hirshfeld surfaces from Crystal Explorer 3.0

Figure S8: Hirshfeld surfaces of four molecules mapped with different properties. Left column (front view) while right column (back view)







Extracted Molecular Pairs

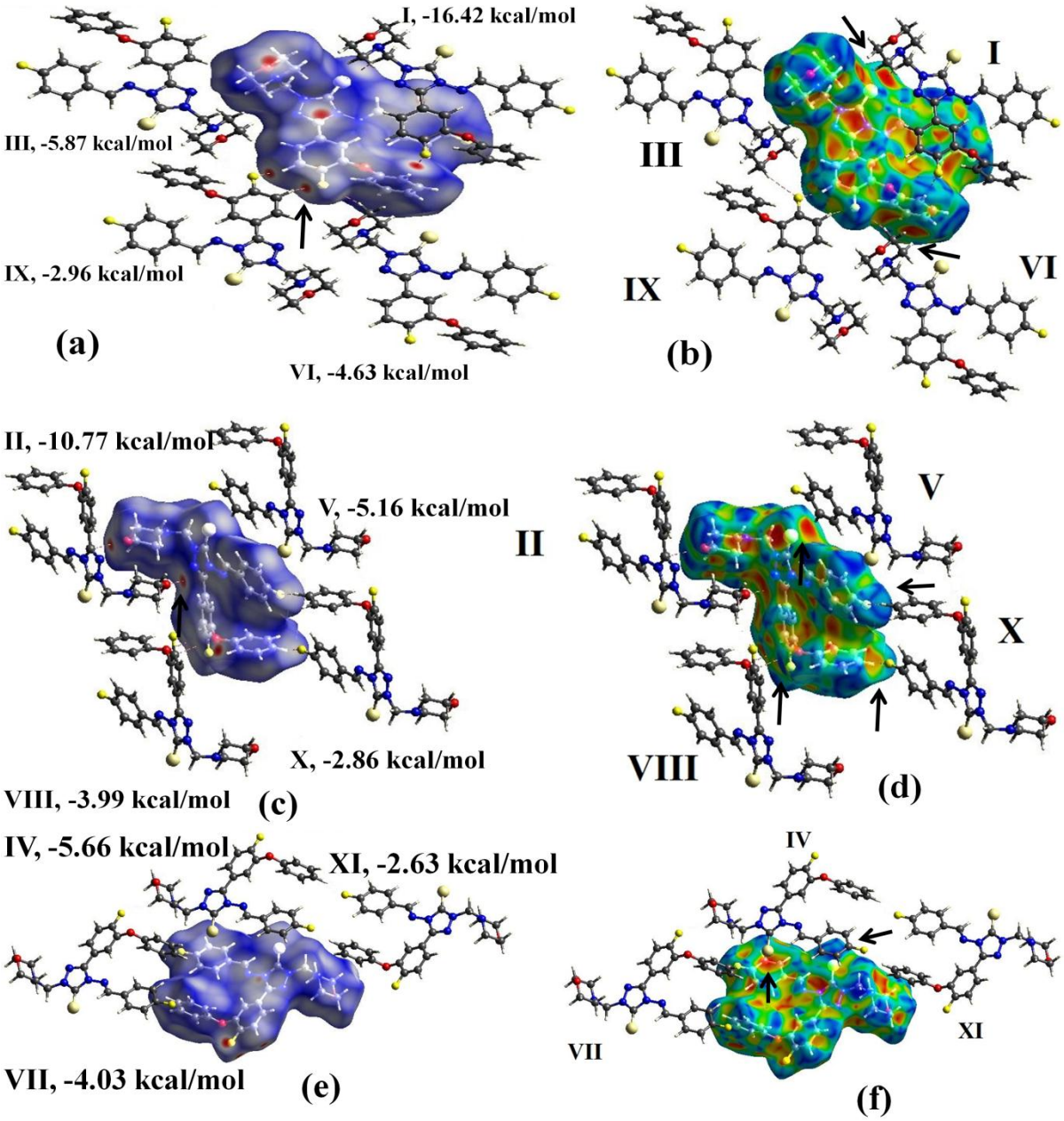


Figure-S9: Hirshfeld surfaces mapped with d_{norm} and shape-index properties along with molecular pairs and their respective PIXEL interaction energies in **TRZ-1**.

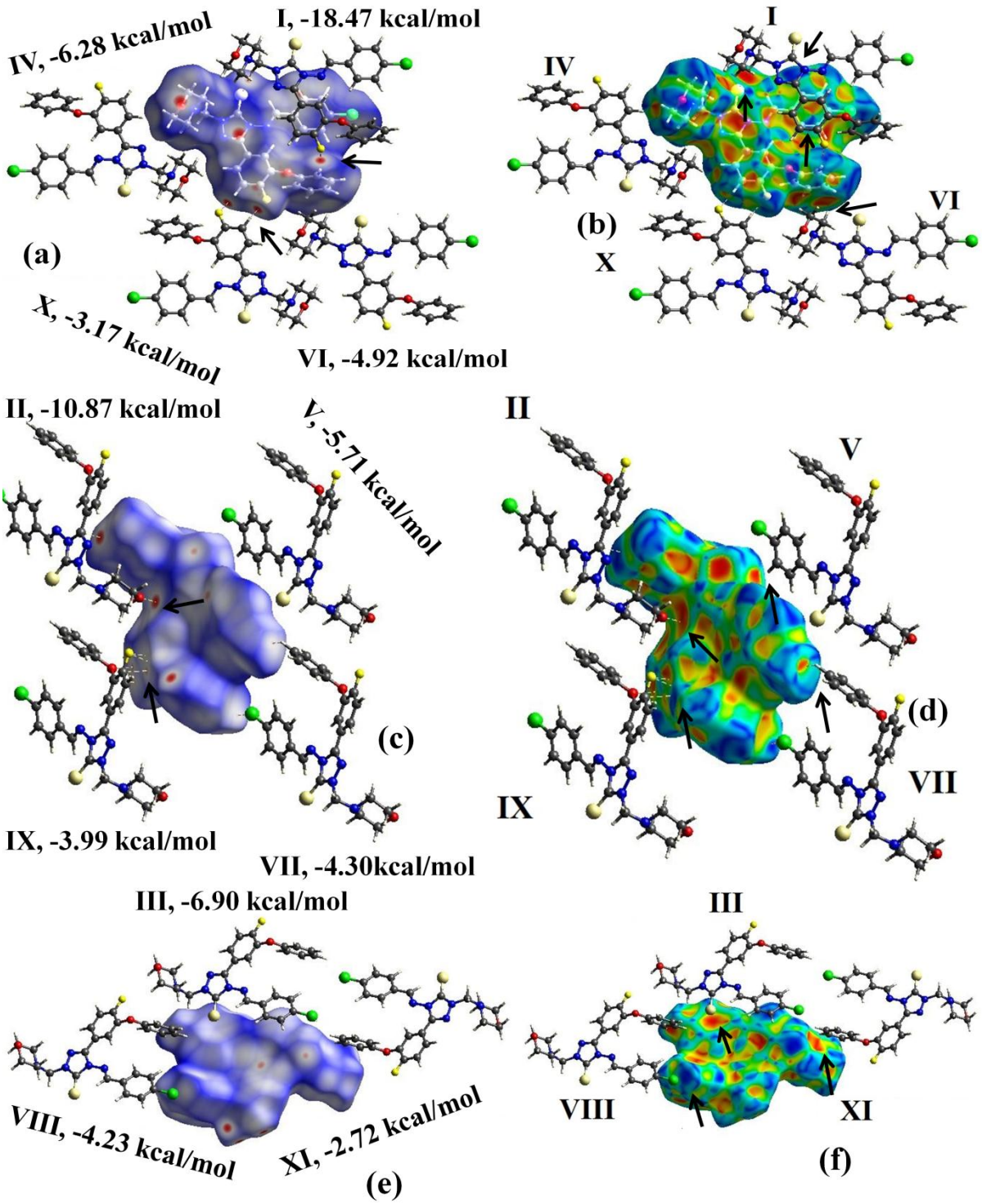


Figure-S10: Hirshfeld surfaces mapped with d_{norm} and shape-index properties along with molecular pairs and their respective PIXEL interaction energies in **TRZ-2A.**

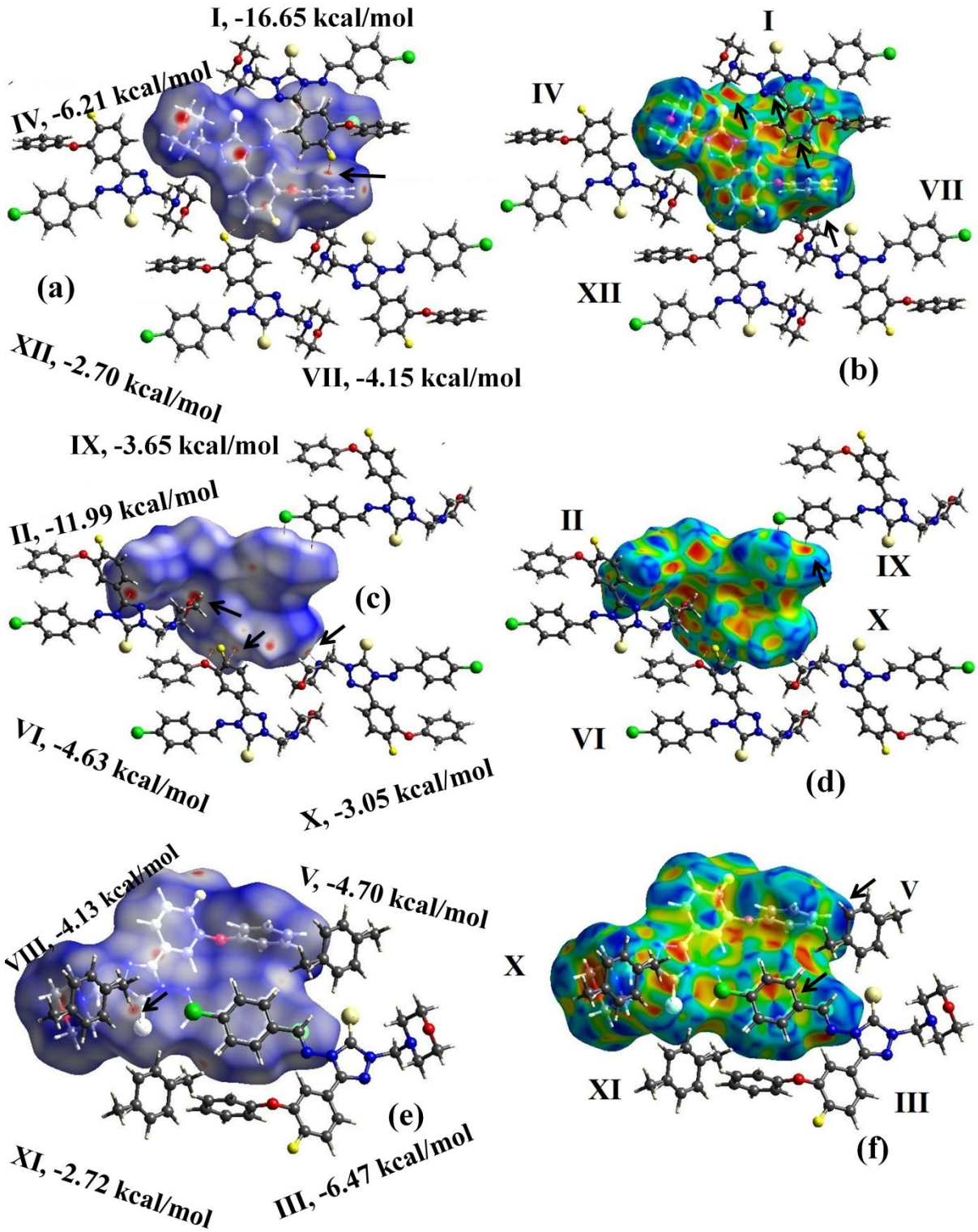
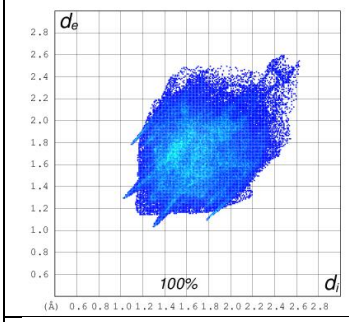
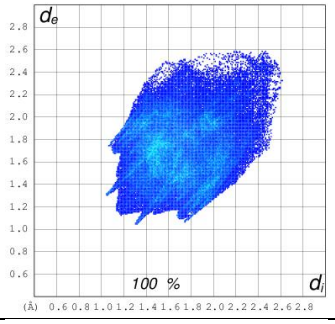
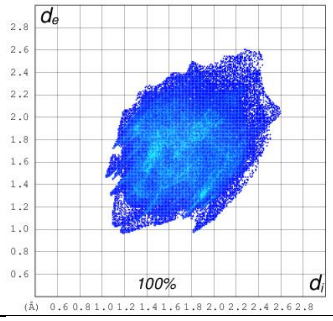
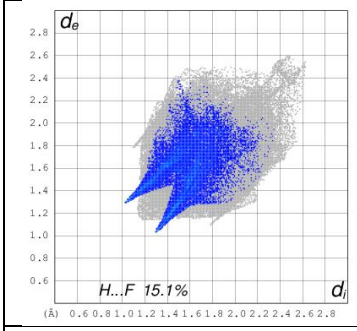
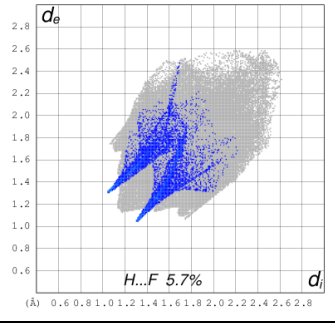
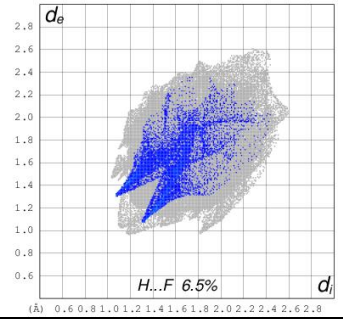
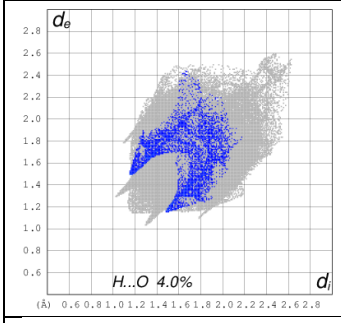
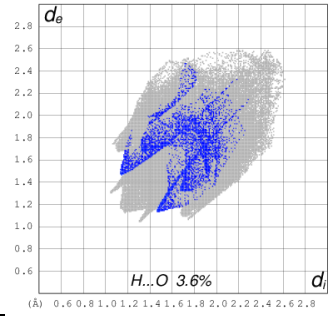
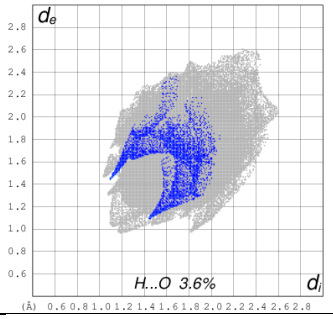
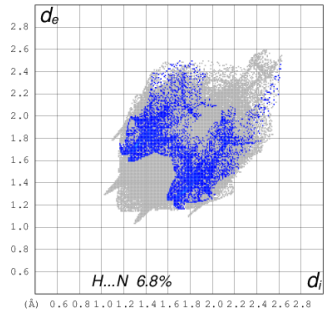
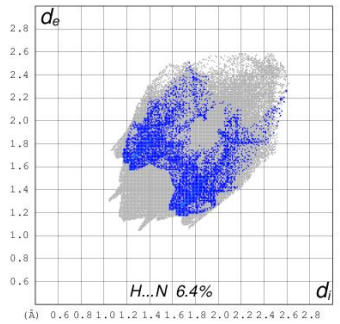
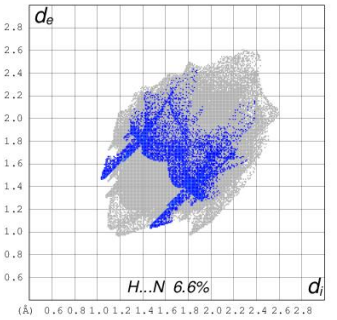
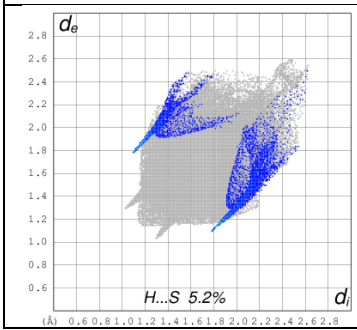
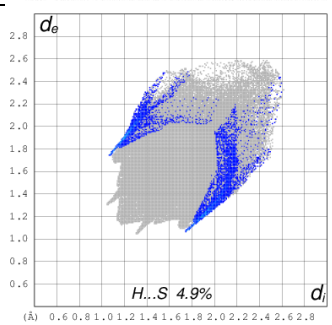
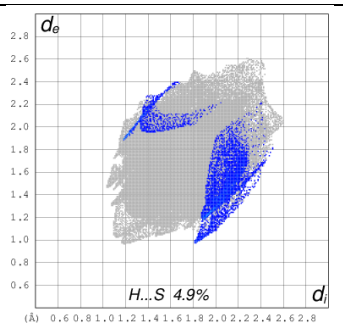


Figure-S11: Hirshfeld surfaces mapped with d_{norm} and shape-index properties along with molecular pairs and their respective PIXEL interaction energies in **TRZ-2B.**

TRZ-1	TRZ-2A	TRZ-2B
		
		
		
		
		

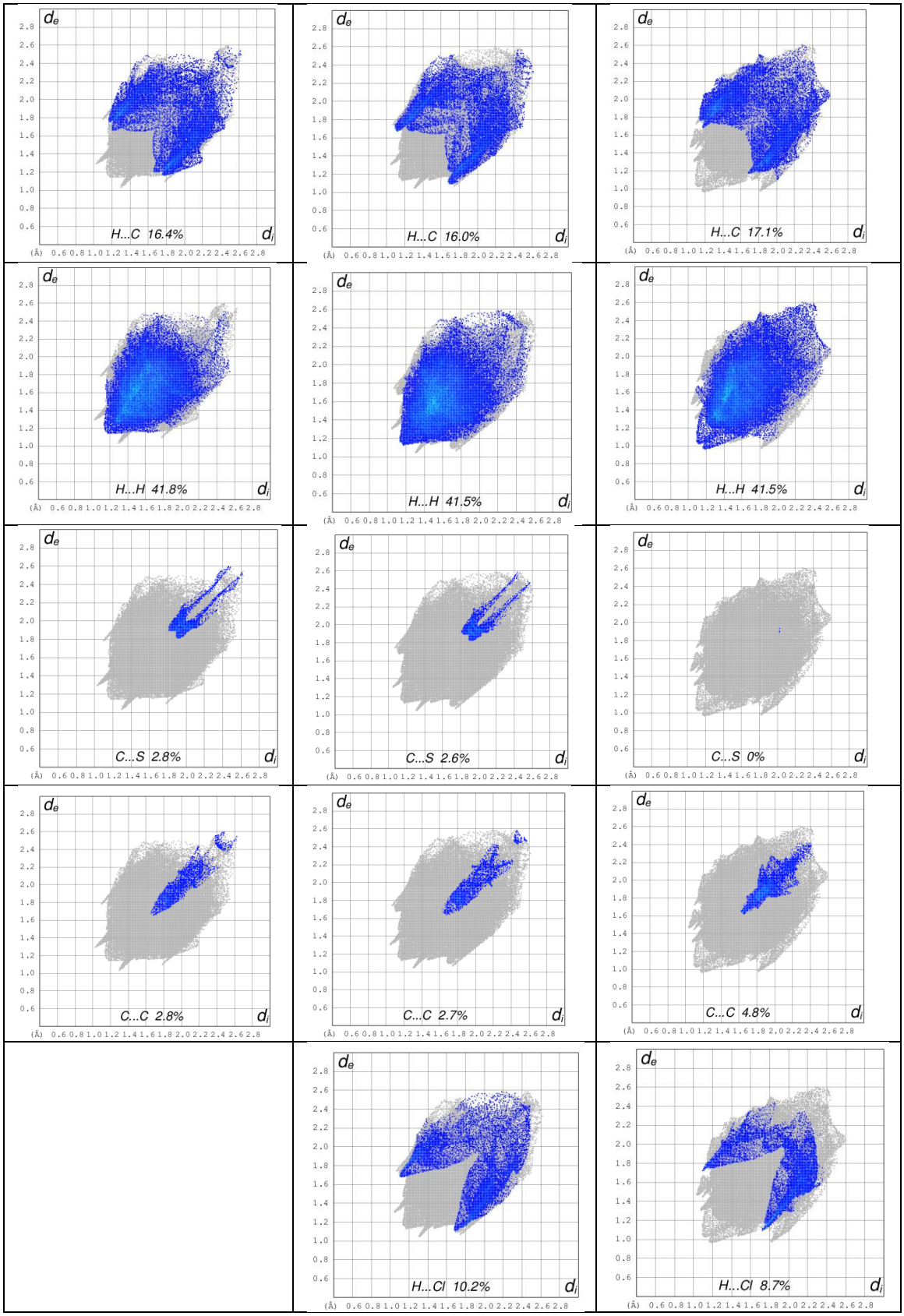


Figure-S12: Comparison of full fingerprint plots of the respective crystal structures and decomposed fingerprint plot for all interacting atoms.

Section-5: Packing Diagram

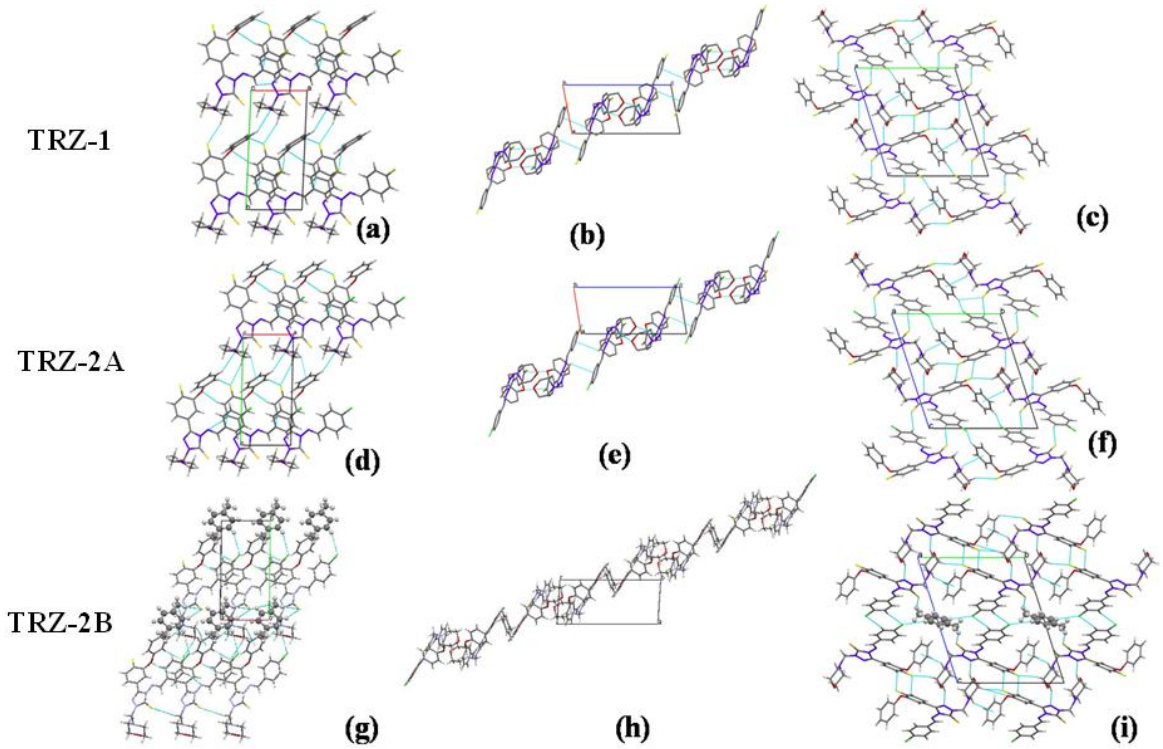
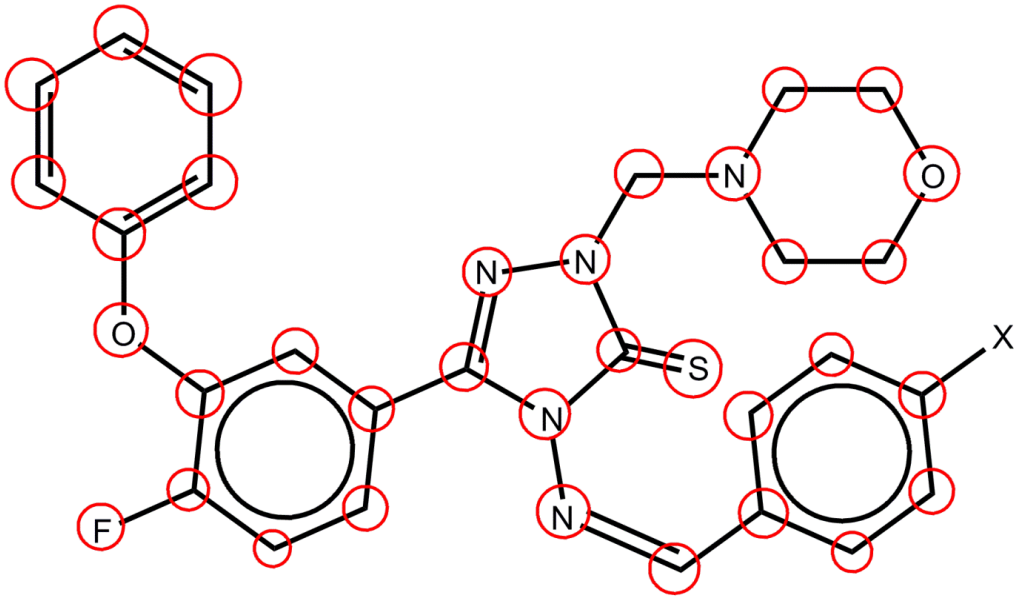


Figure-S13: Crystal packing of (a) **TRZ-1** down the *ab*-plane. (b) **TRZ-1** down the *ac*-plane. (c) **TRZ-1** down the *bc*-plane. (d) **TRZ-2A** down the *ab*-plane. (e) **TRZ-2A** down the *ac*-plane. (f) **TRZ-2A** down the *bc*-plane. (g) **TRZ-2B** down the *ab*-plane. (h) **TRZ-2B** down the *ac*-plane. (i) **TRZ-2B** down the *bc*-plane. The bold lines in cyan indicate intermolecular interactions.

Section-6: XPAC Analysis

XPAC is a computer program to analyse the extent of similarity between two crystal structures. In this program, the components of the two crystal structures to be compared are termed as supramolecular constructs (SC). Supramolecular construct implies geometrical similarity, meaning similarity of two configurations of points rather than similarity in terms of connectivity. XPAC also defines the dissimilarity index 'X' which is a measure of how far the two crystal structures deviate from perfect geometrical similarity. For XPAC analysis, atom circled with label C1-C26, N1-N5, O1-O2 and S1 were considered for **Corresponding Ordered Sets of Points** (COSPs). The filter setting a/p/d: 12/18/1.50 was applied for all the calculations.



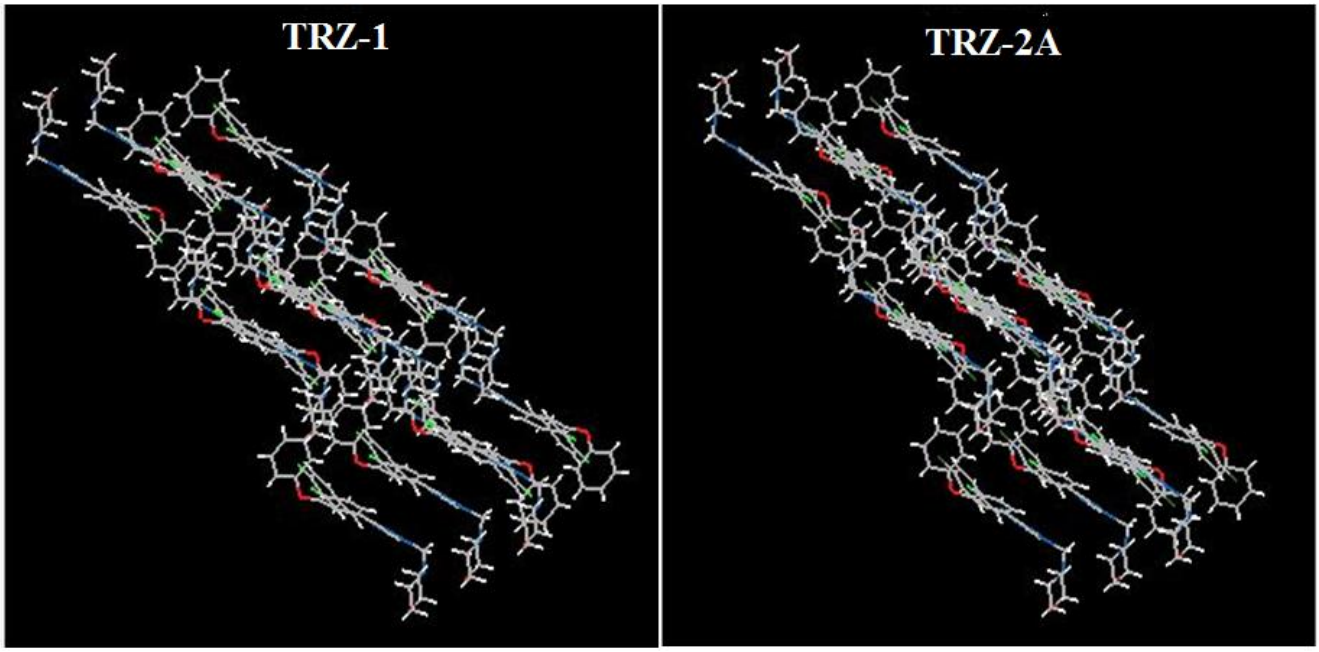


Figure –S14(a): Comparison of the crystal packing between **TRZ-1** and **TRZ-2A** by XPAC depicting 3D SC.

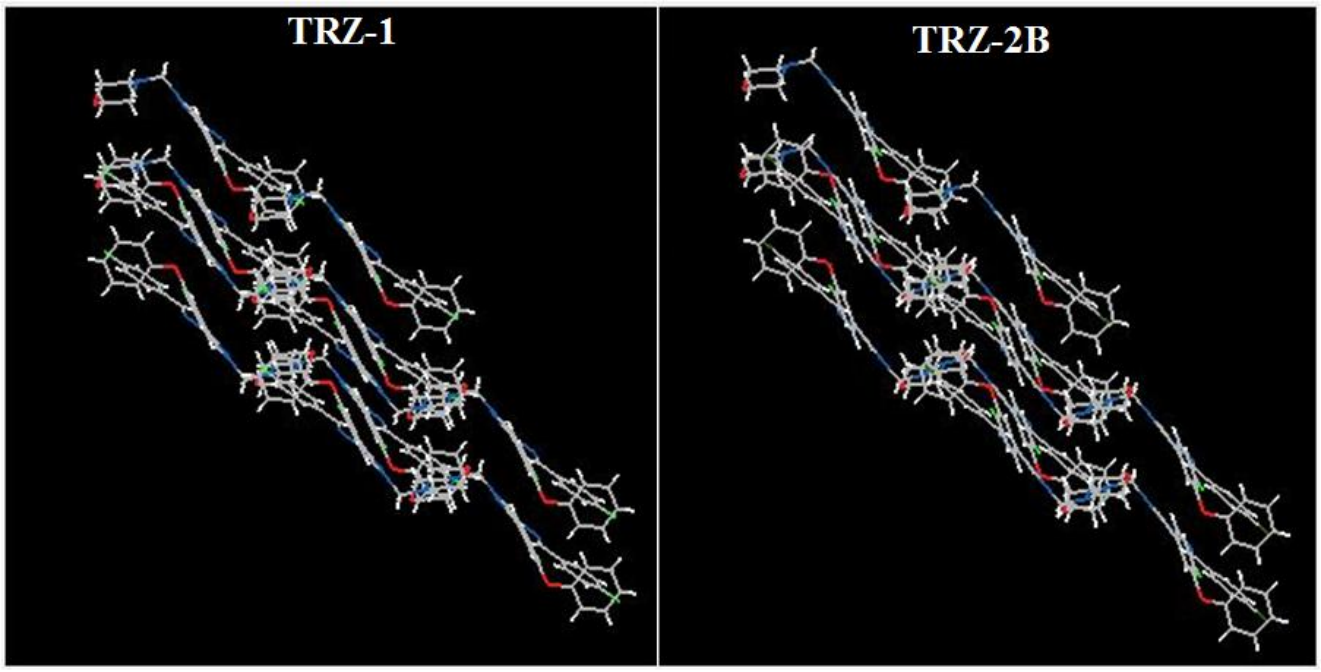


Figure-S14(b): Comparison of the crystal packing between **TRZ-1** and **TRZ-2B** by XPAC depicting 2D SC.

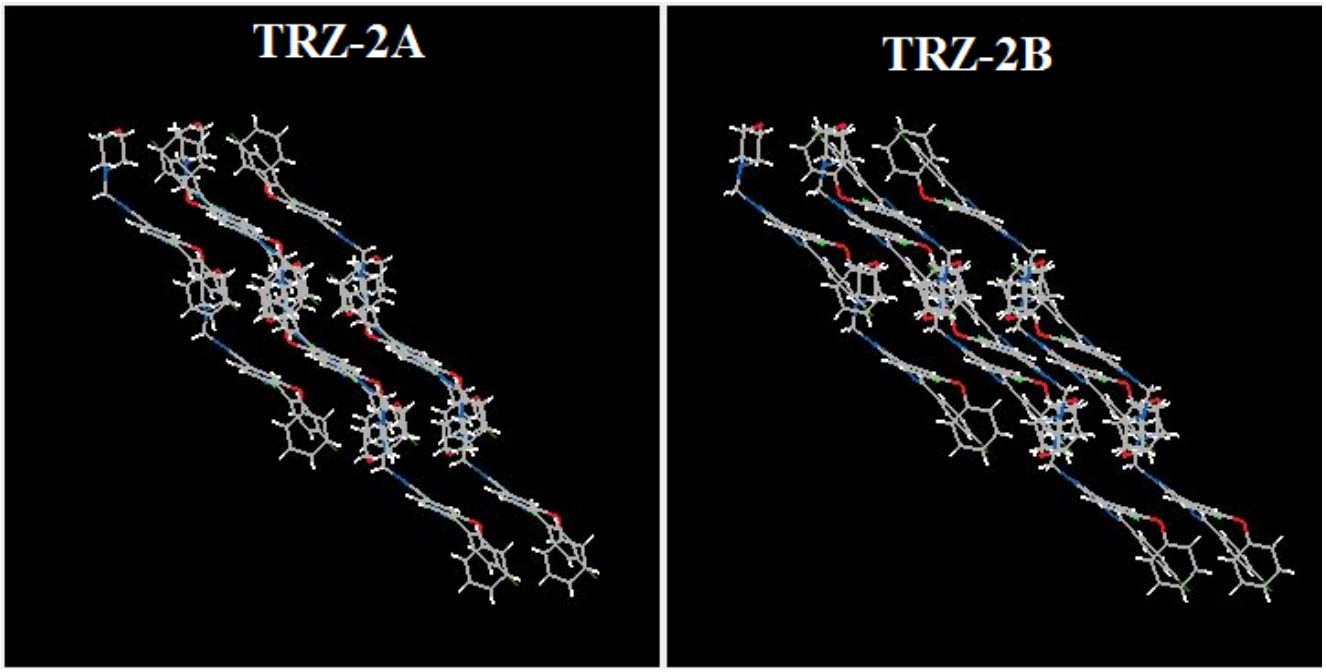


Figure-S14(c): Comparison of crystal packing between **TRZ-2A** and **TRZ-2B** by XPAC depicting 2D SC.

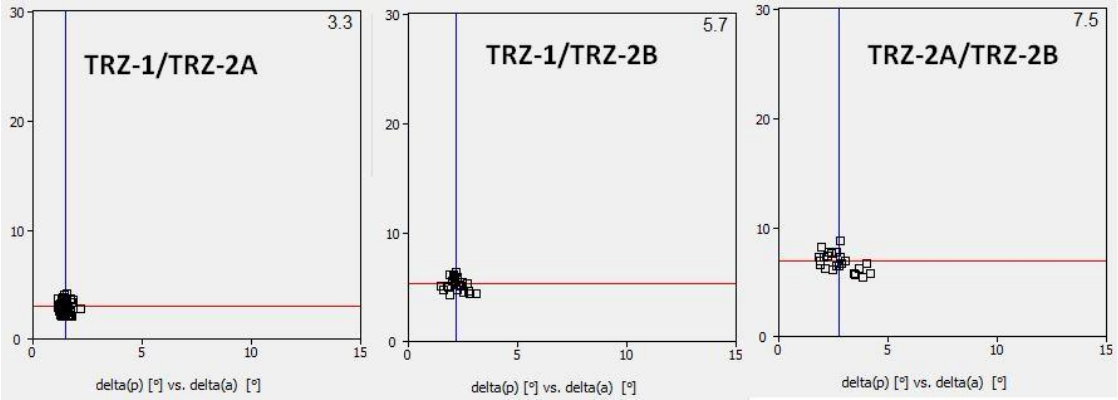


Figure S15(a): XPAC plots δp [y-axis] against δa [x-axis] (both in º), displaying the degree of similarity. Upper right corner is the dissimilarity index X, vertical and horizontal lines are the mean values of δa and δp, respectively.

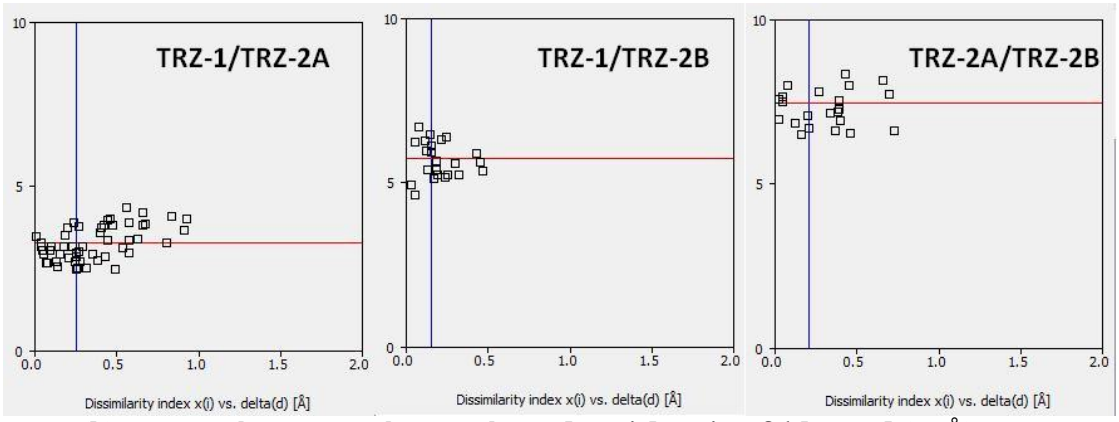


Figure S15:(b): XPAC plots Dissimilarity index X [y-axis] against δd [x-axis] (in Å)

Section 7: TURBOMOLE Calculations

Table-S5: Results from Theoretical Calculations performed using TURBOMOLE.

Molecular motifs	Interaction Energy calculated by DFT+Disp/B97-D/ cc-pVTZ (kcal/mol)	Counter Poise corrected Interaction Energy (kcal/mol)	BSSE (kcal/mol)
TRZ-1			
I	**-19.40**	**-18.21**	**1.19**
II	**-14.30**	**-13.37**	**0.93**
III	**-7.25**	**-6.84**	**0.41**
IV	**-8.29**	**-7.59**	**0.70**
V	**-4.86**	**-4.57**	**0.29**
VI	**-5.78**	**-5.44**	**0.34**
VII	**-4.77**	**-4.43**	**0.34**
VIII	**-3.13**	**-2.89**	**0.24**
IX	**-2.63**	**-2.41**	**0.22**
X	**-3.08**	**-2.89**	**0.19**
XI	**-3.37**	**-3.17**	**0.20**
TRZ-2A			
I	**-20.21**	**-18.94**	**1.27**
II	**-13.91**	**-13.01**	**0.90**

III	**-8.26**	**-7.72**	**0.54**
IV	**-7.69**	**-7.27**	**0.42**
V	**-4.94**	**-4.66**	**0.28**
VI	**-5.92**	**-5.60**	**0.32**
VII	**-2.50**	**-2.33**	**0.17**
VIII	**-4.00**	**-3.75**	**0.25**
IX	**-5.98**	**-5.29**	**0.69**
X	**-2.70**	**-2.48**	**0.22**
XI	**-3.41**	**-3.21**	**0.20**
TRZ-2B			
I	**-18.39**	**-17.26**	**1.13**
II	**-15.57**	**-14.60**	**0.97**
III	**-7.27**	**-6.84**	**0.43**
IV	**-6.83**	**-6.21**	**0.62**
V	**-4.16**	**-3.97**	**0.19**
VI	**-6.66**	**-5.94**	**0.72**
VII	**-5.42**	**-5.11**	**0.31**
VIII	**-4.54**	**-4.32**	**0.22**
IX	**-2.15**	**-2.01**	**0.14**
X	**-3.83**	**-3.61**	**0.22**
XI	**-2.87**	**-2.68**	**0.19**
XII	**-2.81**	**-2.59**	**0.22**