Non-covalent interactions involving remote substituents influence the topologies of supramolecular chains featuring hydroxyl-O–H···O(hydroxyl) hydrogen bonding in crystals of (4-YC_6H_4)N(H)C(=S)N(CH_2CH_2OH)$_2$ for Y = H, Me, Cl and NO_2

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Electronic Supplementary Information

Table S1. A listing of selected electrostatic potentials and charge deviations (ΔV_{ESP}) for molecules **1**-**4**.

Table S2. List of natural charges for **1**-**4**.

Table S3 The d_{norm} contact distances for all interactions with $d_i + d_e < \Sigma$(van der Waals radii) in **1**-**4** as determined through Hirshfeld surface analysis, with all X–H bond lengths adjusted to their neutron values.

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Figure S3 Crystallographic diagrams for **3**: Side-on and end-on views of the supramolecular chain sustained by hydroxyl-O–H···O(hydroxyl) hydrogen bonding, shown as orange dashed lines.

Figure S4 The overall two-dimensional fingerprint plots and selected decomposed fingerprint plots delineated into H···O/O···H, H···C/C···H and H···S/S···H surface contacts for (a) **1a**, (b) **1b**, (c) **2**, (d) **3**, (e) **4a** and (f) **4b**, with the internal/external percentage contributions specified for each contact.

Figure S5 Molecular topology obtained through QTAIM analysis, showing the bond critical point (orange dot) and ring critical point (yellow dot) for C–H···π(C=S) interactions present in (a) **2**, (b) **3** and (c) **4**. The embedded diagram shows the corresponding NCI plot of the interaction for the corresponding pairwise molecules. The analogous C–H···π(C=S) interaction is absence in **1** and hence, the topology is not shown.

Figure S6 NCI plots for the molecular dimers of (a) **1**, (b) **2**, (c) **3** and (d) **4** featuring complementary interactions involving C–H···O, C–H···π or C–H···C contacts.

Table S1. A listing of selected electrostatic potentials and charge deviations (ΔV_{ESP}) for molecules **1**-**4**.

Contact	V_{ESP} (kcal/mol)		
	H-donor	H-acceptor	ΔV_{ESP}
1			
O1–H1o···O2	+55.73	-42.01	97.74
C8–H8a···S1	+29.03	-36.09	65.12
C4–H4···S1	+5.92	-35.13	41.05
2			
O1–H1o···O2	+55.99	-42.45	98.44
C6–H6···O2	+12.07	-45.78	57.85
3			
O1–H1o···O2	+59.12	-39.60	98.72
C6–H6···O2	+13.38	-40.42	53.80
C10–H10b···Cl1	+33.16	+0.76	32.40
Cl1···Cl1	-0.94	-0.94	-1.88
4			
O1–H1o···O2	+59.49	-39.30	98.79
C10–H10a···S1	+36.24	-30.37	66.61
C11–H11b···O3	+12.52	-36.91	49.43
C7–H7···O3	+10.23	-34.49	44.72

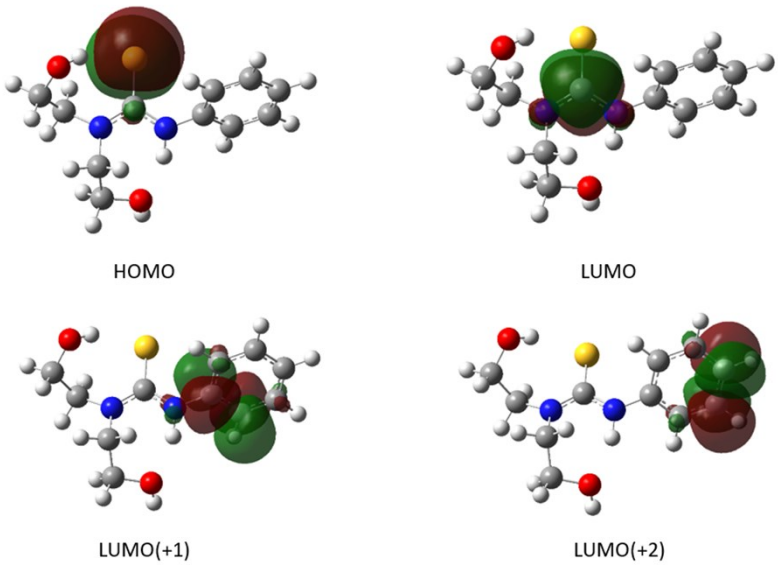
Table S2. List of natural charges for **1**-**4**.

Atom	Natural Charge, |e|			
	1	**2**	**3**	**4**
S1	-0.393	-0.397	-0.387	-0.361
O1	-0.737	-0.737	-0.737	-0.736
H1O	0.496	0.496	0.496	0.498
O2	-0.748	-0.749	-0.747	-0.743
H2O	0.480	0.480	0.480	0.480
N1	-0.613	-0.611	-0.613	-0.614
H1N	0.444	0.444	0.445	0.448
N2	-0.396	-0.397	-0.393	-0.384
C1	0.345	0.346	0.344	0.338
C2	0.141	0.126	0.141	0.195
C3	-0.215	-0.205	-0.197	-0.222
C4	-0.208	-0.212	-0.224	-0.169
C5	-0.226	-0.024	-0.053	-0.010
C6	-0.205	-0.209	-0.222	-0.164
C7	-0.234	-0.224	-0.216	-0.235
C8	-0.249	-0.249	-0.249	-0.25
C9	-0.08	-0.08	-0.08	-0.08
C10	-0.25	-0.249	-0.25	-0.251
C11	-0.075	-0.075	-0.075	-0.075
C5'	-	-0.624	-	-
Cl1	-	-	-0.011	-
O3	-	-	-	-0.398
O4	-	-	-	-0.399
N3	-	-	-	0.532
H3	0.23	0.229	0.237	0.245
H4	0.222	0.218	0.237	0.252
H5	0.222	-	-	-
H6	0.223	0.218	0.238	0.252
H7	0.225	0.224	0.232	0.235
H8a	0.224	0.223	0.224	0.226
H8b	0.227	0.227	0.228	0.229
H9a	0.182	0.18	0.181	0.182
H9b	0.181	0.181	0.182	0.184
H10a	0.233	0.233	0.234	0.234
H10b	0.216	0.216	0.217	0.219
H11a	0.169	0.169	0.17	0.171
H11b	0.17	0.17	0.17	0.171
H5a'	-	0.222	-	-
H5b'	-	0.22	-	-
H5c'	-	0.221	-	-

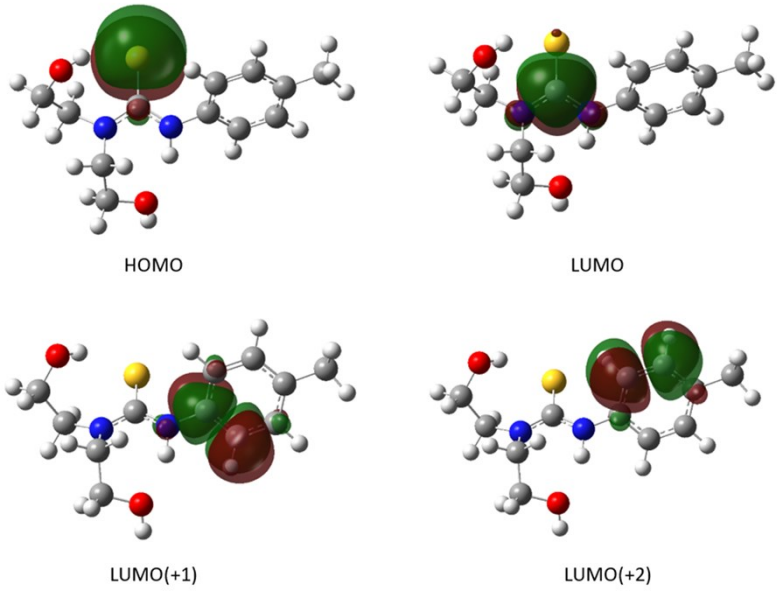
Table S3 The d_{norm} contact distances for all interactions with $d_i + d_e < \Sigma$(van der Waals radii) in **1**-**4** as determined through Hirshfeld surface analysis, with all X–H bond lengths adjusted to their neutron values.

Type	Contact	Distance (Å)	Symmetry operation
1			
I	H1o···O22	1.70	*x*, *y*, *z*
I	H21o···O2	1.70	*x*, *y*, 1+*z*
I	H28b···O1	2.54	1-*x*, 1-*y*, 1-*z*
I	H5···O1	2.54	1½-*x*, ½+*y*, ½-*z*
II	H9a···C22	2.68	1-*x*, 1-*y*, 1-*z*
II	H9a···C23	2.70	1-*x*, 1-*y*, 1-*z*
II	H29b···C7	2.71	-½+*x*, ½-*y*, ½+*z*
II	H29a···C7	2.73	1-*x*, 1-*y*, 1-*z*
III	H4···S21	2.85	1½-*x*, ½+*y*, ½-*z*
III	H8a···S21	2.83	-½+*x*, ½-*y*, -½+*z*
IV	C21···O22	3.19	1-*x*, 1-*y*, 1-*z*
2			
I	H1o···O2	1.74	-½-*x*, -½+*y*, 1½-*z*
I	H6···O2	2.55	½-*x*, -½+*y*, 1½-*z*
II	H10b···C6	2.65	-½+*x*, ½-*y*, -½+*z*
II	H9a···C7	2.71	-1+*x*, *y*, *z*
II	H4···C10	2.74	½-*x*, ½+*y*, 1½-*z*
3			
I	H1o···O2	1.73	-½-*x*, ½+*y*, ½-*z*
I	H6···O2	2.51	½-*x*, ½+*y*, ½-*z*
II	H10a···C6	2.67	-½+*x*, 1½-*y*, -½+*z*
II	H4···C10	2.73	½-*x*, -½+*y*, ½-*z*
II	H9b···C7	2.75	-1+*x*, *y*, *z*

II	H8a···C5	2.78	-1+*x*, *y*, *z*
V	H10b···Cl1	2.78	-1½+*x*, 1½-*y*, -½+*z*
V	Cl1···Cl1	3.44	2-*x*, 1-*y*, 1-*z*
4			
I	H1o···O22	1.75	*x*, 1+*y*, *z*
I	H21o···O2	1.76	*x*, *y*, *z*
I	H29b···O1	2.29	-*x*, 1-*y*, 1-*z*
I	H11b···O3	2.30	*x*, *y*, 1+*z*
I	H7···O23	2.53	*x*, 1+*y*, -1+*z*
I	H27···O3	2.55	*x*, *y*, 1+*z*
I	H31a···O23	2.56	*x*, *y*, -1+*z*
II	H30a···C5	2.73	1-*x*, 1-*y*, 1-*z*
II	H30a···C4	2.75	1-*x*, 1-*y*, 1-*z*
II	H10b···C24	2.76	1-*x*, 1-*y*, 2-*z*
III	H30b···S1	2.83	1-*x*, 1-*y*, 1-*z*
III	H10a···S21	2.86	1-*x*, 1-*y*, 2-*z*



(a)



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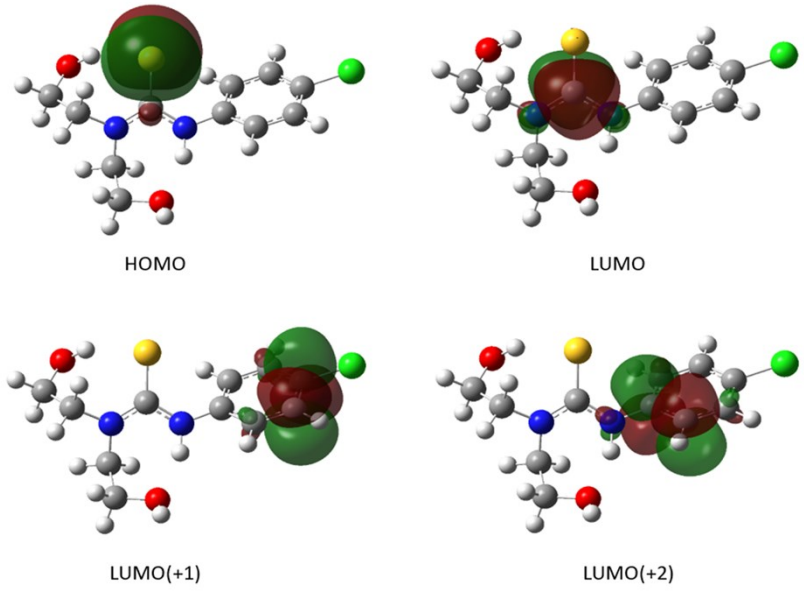

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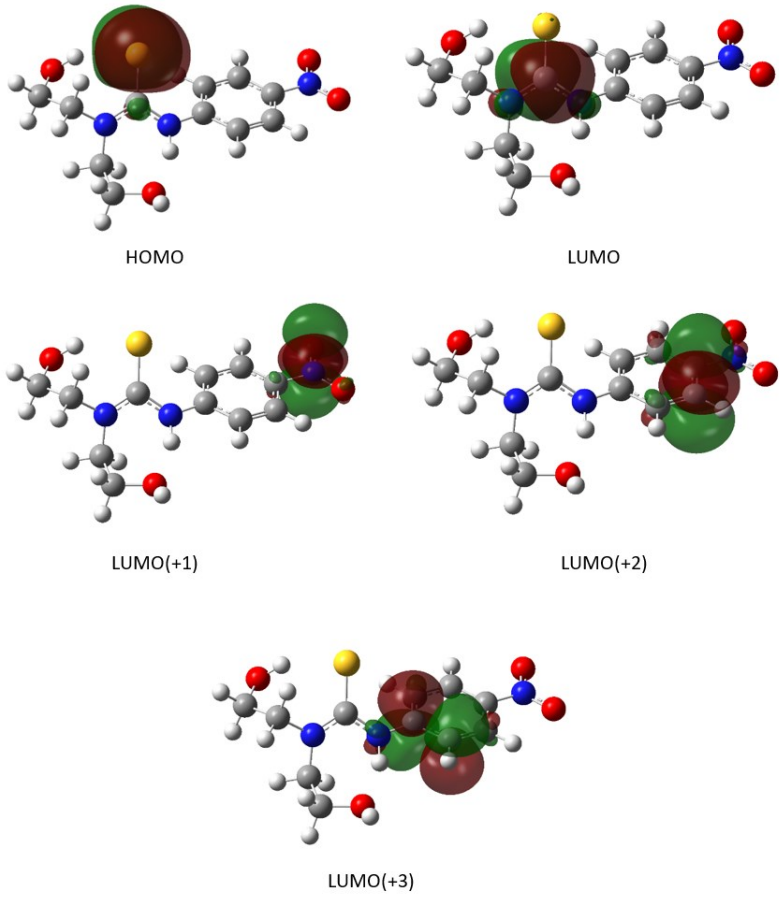
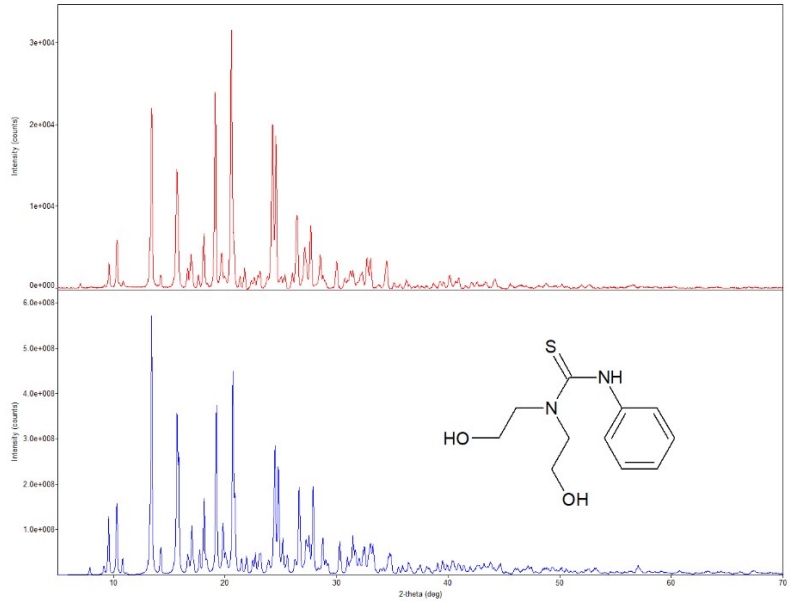


(d)

Figure S1 HOMO-LUMO mapping for (a) **1**, (b) **2**, (c) **3** and (d) **4**.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1e+004
0e+000
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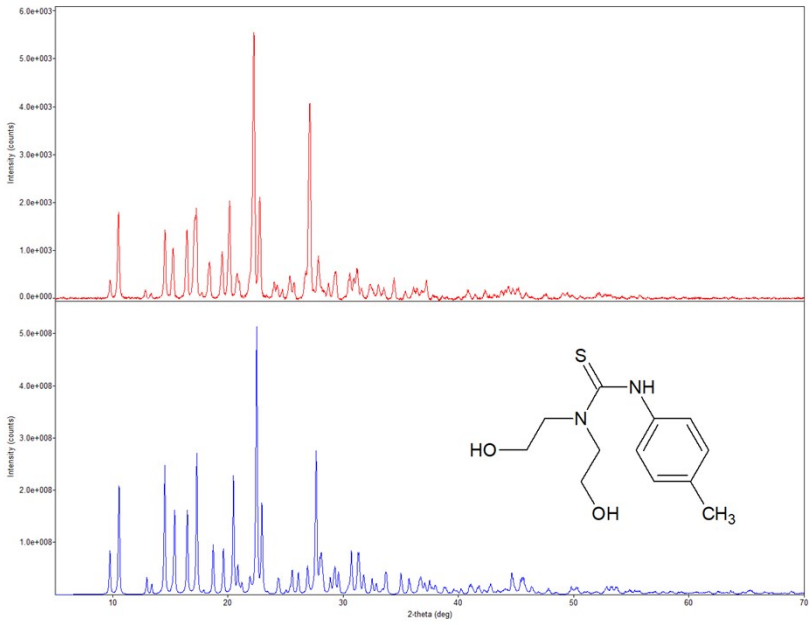
5.0e+008
4.0e+008
3.0e+008
2.0e+008
1.0e+008
10
20
30
40
50
60
70
2-theta (deg)
S
NH
N
HO
OH

(a)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5.0e+003
4.0e+003
3.0e+003
2.0e+003
1.0e+003
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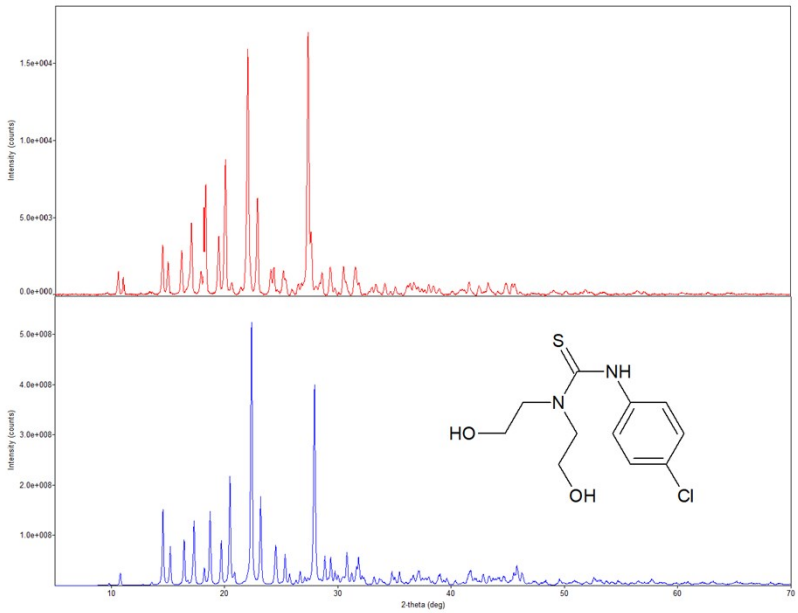
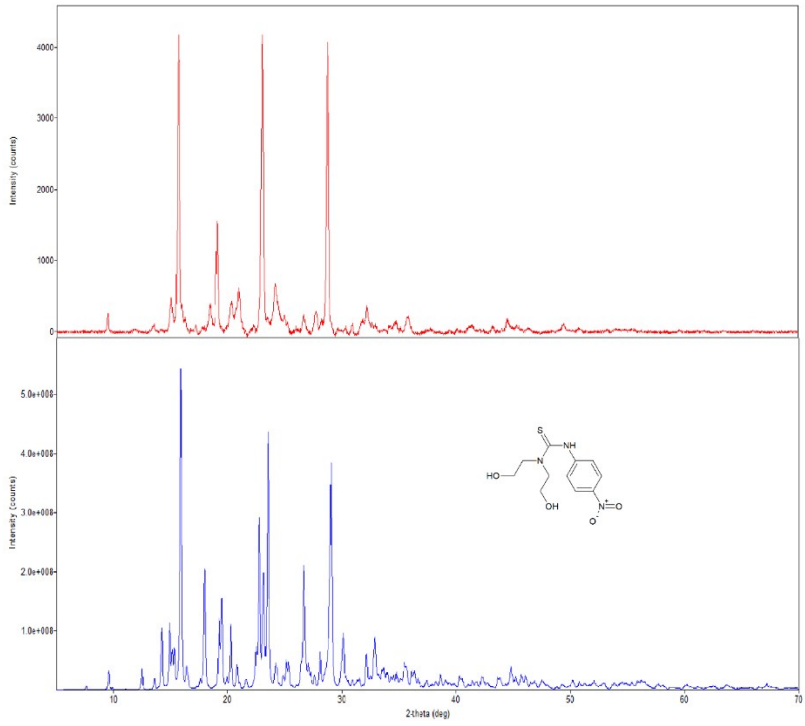
5.0e+008
4.0e+008
3.0e+008
2.0e+008
1.0e+008
10
20
30
40
50
60
70
2-theta (deg)
S
NH
N
HO
OH
CH3

(b)



(c)



(d)

Figure S2 Comparison of the simulated (blue) and experimental (red) PXRD patterns for (a) **1**, (b) **2**, (c) **3** and (d) **4**.

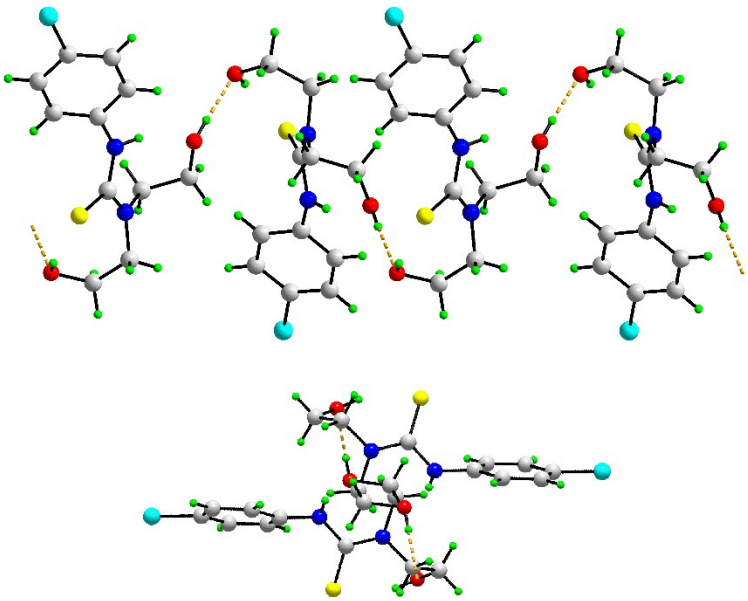


Figure S3 Crystallographic diagrams for **3**: (a) Side-on and end-on views of the supramolecular chain sustained by hydroxyl-O–H···O(hydroxyl) hydrogen bonding, shown as orange dashed lines.

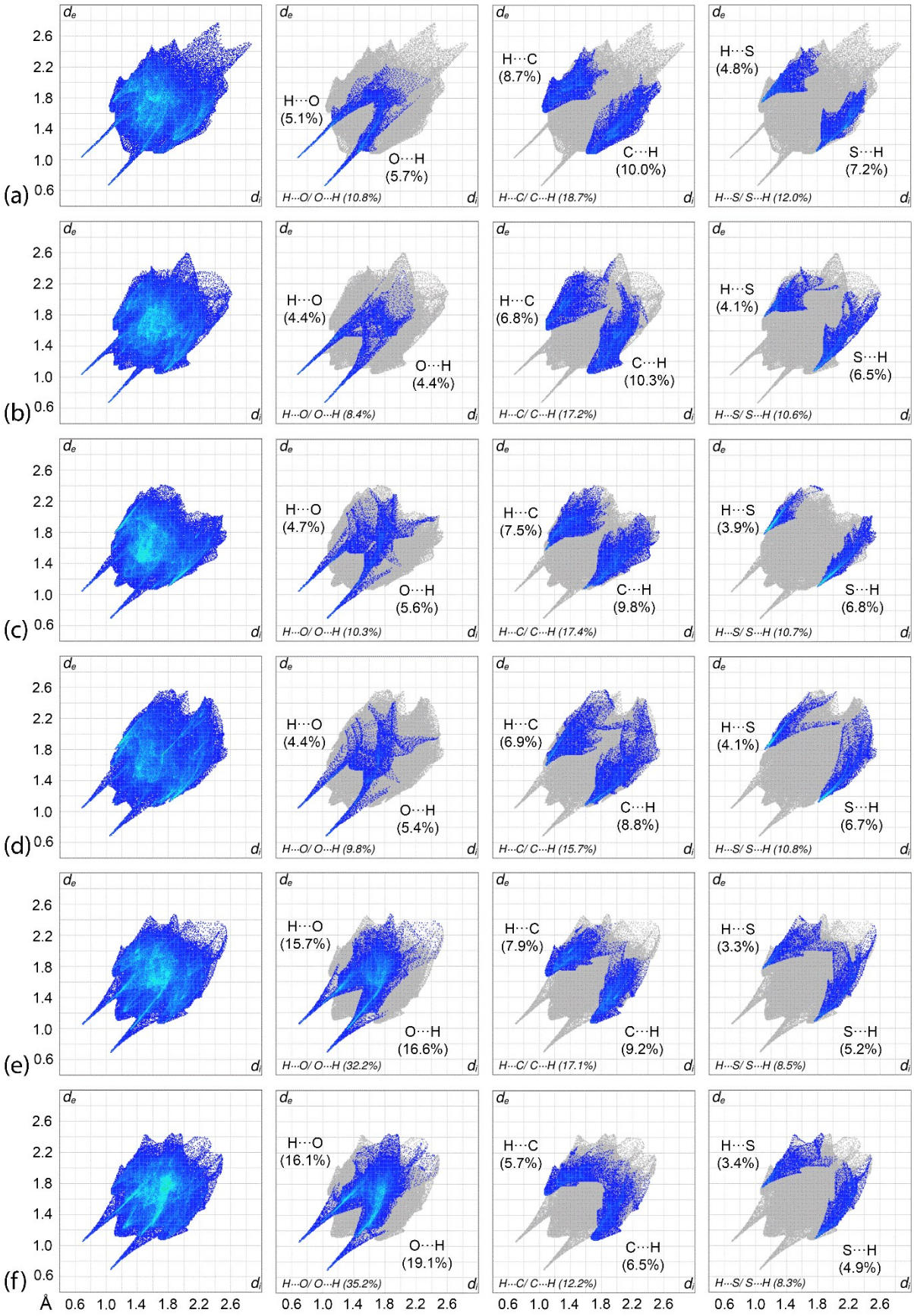

(a)
(b)
(c)
(d)
(e)
(f)
d_e
d_i
2.6
2.2
1.8
1.4
1.0
0.6
H···O (5.1%)
O···H (5.7%)
H···O/ O···H (10.8%)
H···C (8.7%)
C···H (10.0%)
H···C/ C···H (18.7%)
H···S (4.8%)
S···H (7.2%)
H···S/ S···H (12.0%)
H···O (4.4%)
O···H (4.4%)
H···O/ O···H (8.4%)
H···C (6.8%)
C···H (10.3%)
H···C/ C···H (17.2%)
H···S (4.1%)
S···H (6.5%)
H···S/ S···H (10.6%)
H···O (4.7%)
O···H (5.6%)
H···O/ O···H (10.3%)
H···C (7.5%)
C···H (9.8%)
H···C/ C···H (17.4%)
H···S (3.9%)
S···H (6.8%)
H···S/ S···H (10.7%)
H···O (4.4%)
O···H (5.4%)
H···O/ O···H (9.8%)
H···C (6.9%)
C···H (8.8%)
H···C/ C···H (15.7%)
H···S (4.1%)
S···H (6.7%)
H···S/ S···H (10.8%)
H···O (15.7%)
O···H (16.6%)
H···O/ O···H (32.2%)
H···C (7.9%)
C···H (9.2%)
H···C/ C···H (17.1%)
H···S (3.3%)
S···H (5.2%)
H···S/ S···H (8.5%)
H···O (16.1%)
O···H (19.1%)
H···O/ O···H (35.2%)
H···C (5.7%)
C···H (6.5%)
H···C/ C···H (12.2%)
H···S (3.4%)
S···H (4.9%)
H···S/ S···H (8.3%)
Å
0.6 1.0 1.4 1.8 2.2 2.6

Figure S4 The overall two-dimensional fingerprint plots and selected decomposed fingerprint plots delineated into H···O/O···H, H···C/C···H and H···S/S···H surface contacts for (a) **1a**, (b) **1b**, (c) **2**, (d) **3**, (e) **4a** and (f) **4b**, with the internal/external percentage contributions specified for each contact.

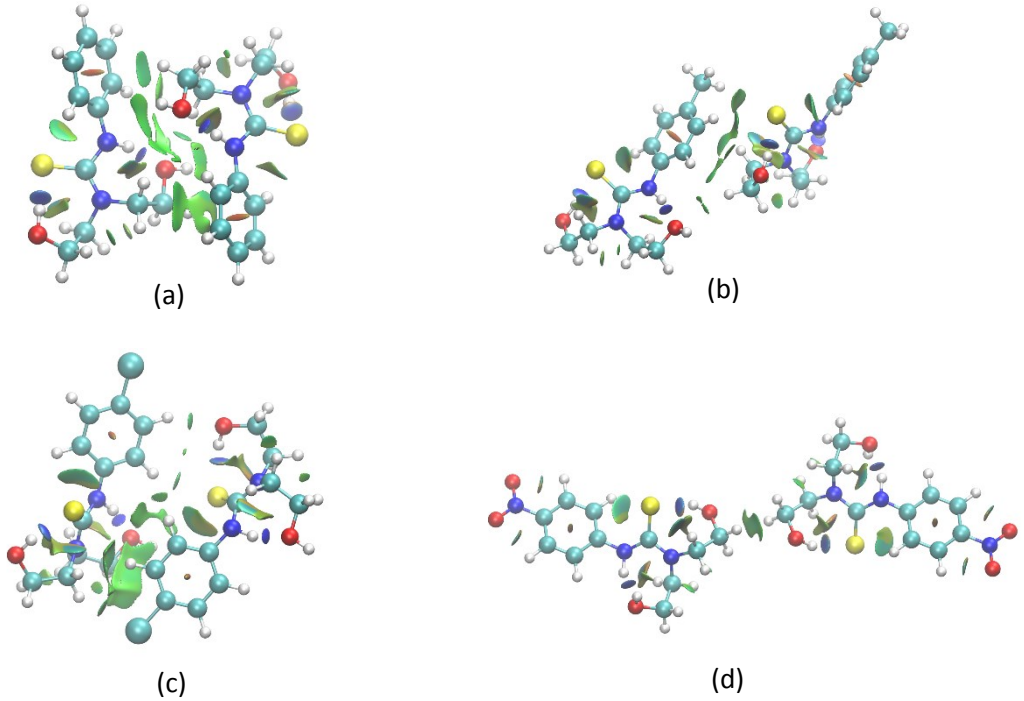


Figure S5 NCI plots for the molecular dimers of (a) **1**, (b) **2**, (c) **3** and (d) **4** featuring the complementary interactions involving C–H···O, C–H···π or C–H···C contacts.

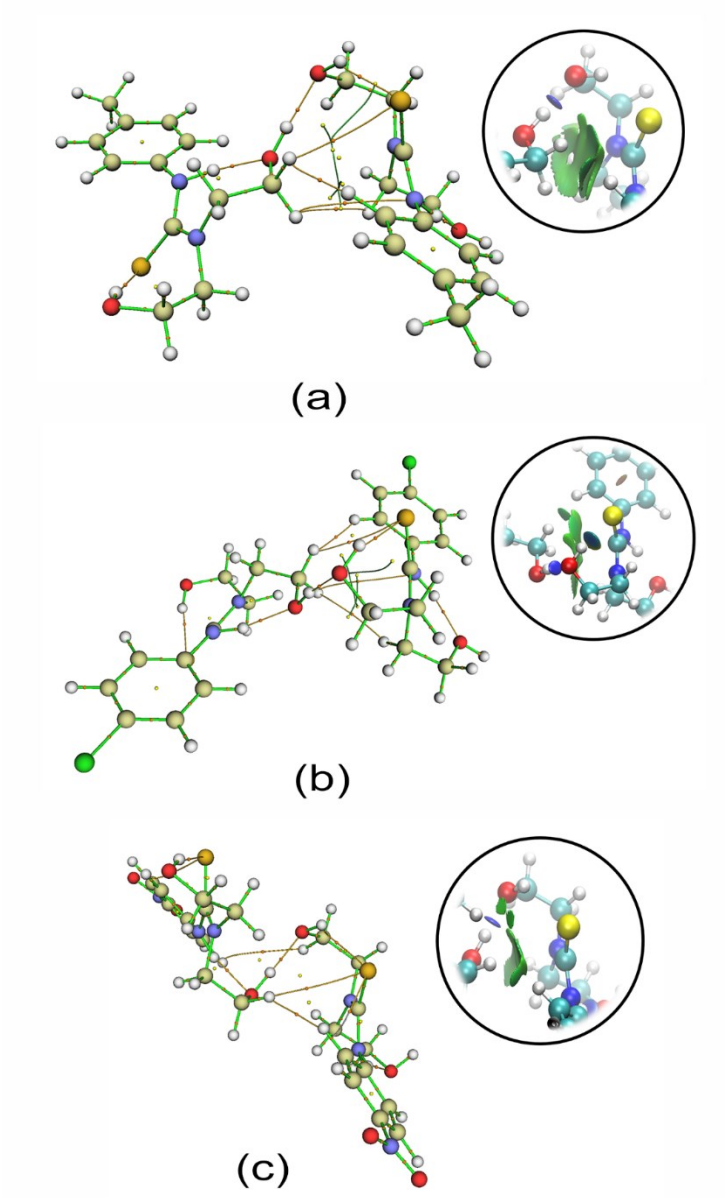


Figure S6 Molecular topology obtained through QTAIM analysis, showing the bond critical point (orange dot) and ring critical point (yellow dot) for C–H···π(C=S) interactions present in (a) **2**, (b) **3** and (c) **4**. The embedded diagram shows the corresponding NCI plot of the interaction for the corresponding pairwise molecules. The analogous C–H···π(C=S) interaction is absence in **1** and hence, the topology is not shown.