

Supporting information

Separation or union of non-covalently linked partners provide polymorphs of N-(Aryl)-2-(propan-2-ylidene)hydrazine carbothioamides

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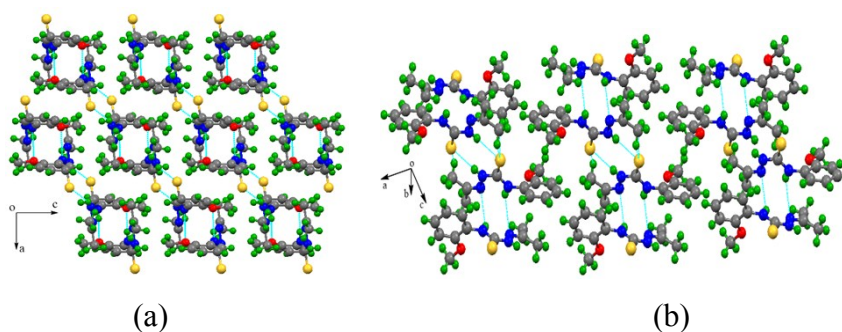


Figure S1: Packing diagrams of polymorph (a) **Methoxypoly1** and (b) **Methoxypoly2**.

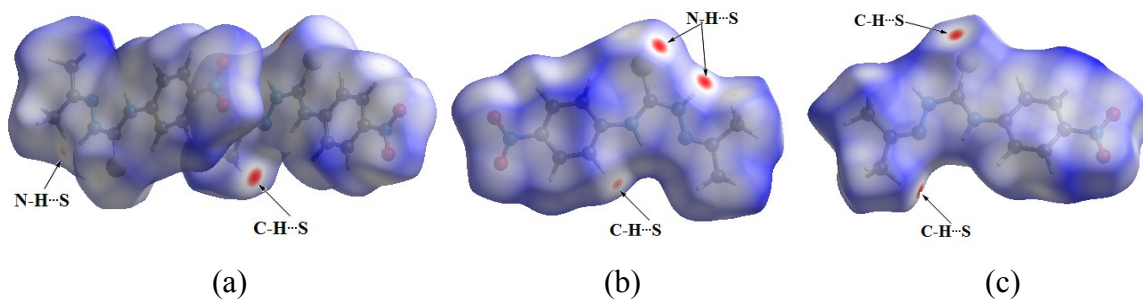
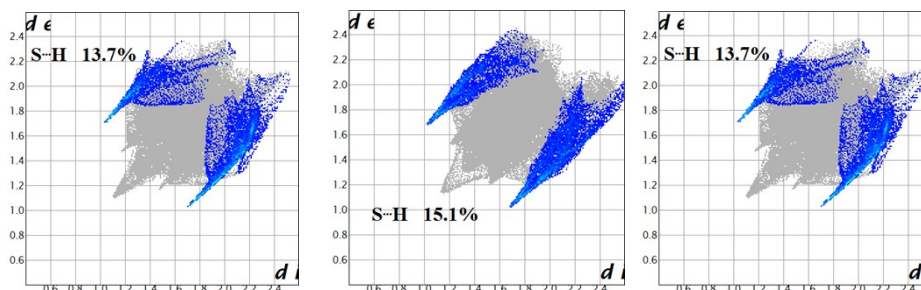


Figure S2: Hirshfeld surface analysis of (a) **Nitropoly1**, (b) **Nitropoly2** and (c) **Nitropoly3** showing d_{norm} surfaces with different hydrogen bonding interactions.



(a) (b) (c)

Figure S3: Fingerprint plots for (a) **Nitropoly1**, (b) **Nitropoly2** and (c) **Nitropoly3** with S...H interactions highlighted in colour.

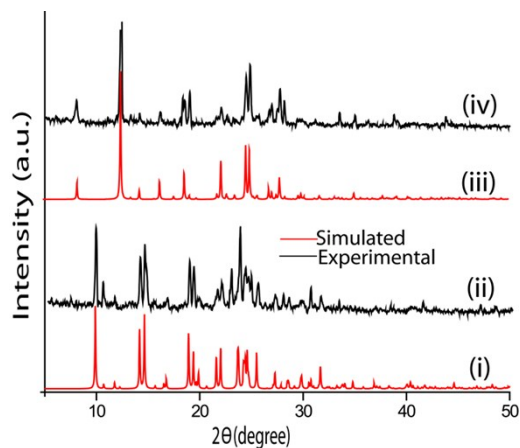


Figure S4: Simulated (i and iii) and experimental (ii and iv) powder X-ray diffraction patterns of polymorph **Methoxypoly1** and **Methoxypoly2** respectively.

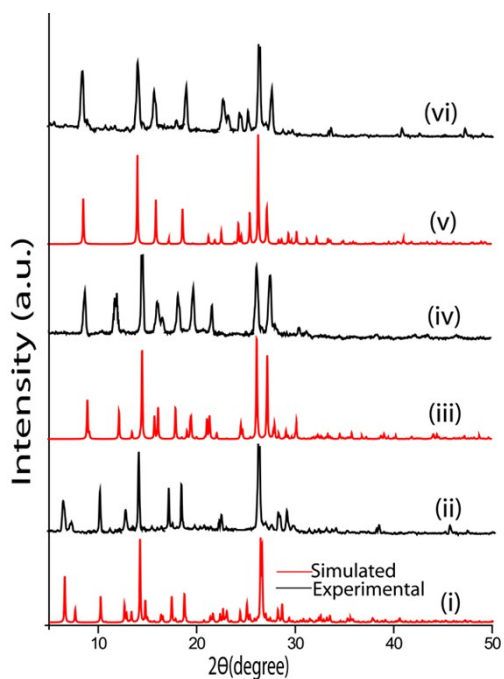


Figure S5: Simulated (i, iii and v) and experimental (ii, iv and vi) powder X-ray diffraction patterns of polymorph **Nitropoly1**, **Nitropoly2** and **Nitropoly3** respectively.

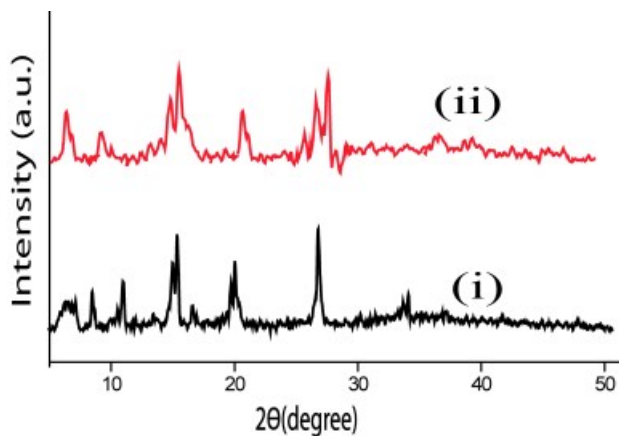


Figure S6: Experimental powder X-ray diffraction patterns of (i) crude compound H_2L_1 and (ii) polymorph **Nitropoly1** after heating to 200 °C.

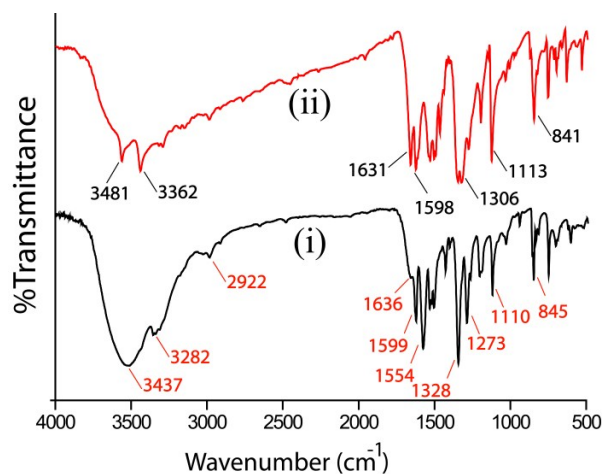


Figure S7: FTIR spectra of (i) crude compound H_2L_1 and (ii) polymorph **Nitropoly1** after heating to 200 °C.

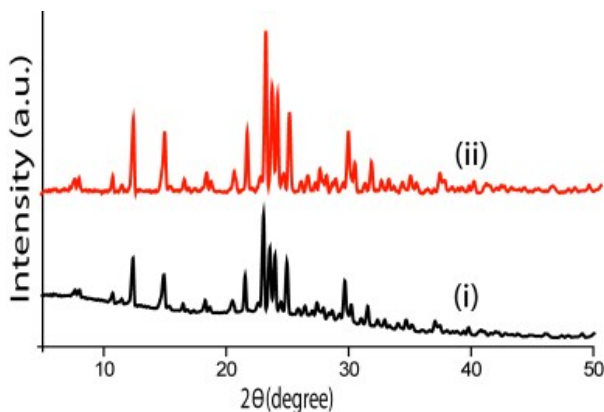


Figure S8: Experimental powder X-ray diffraction patterns of (i) crude compound **H₂L** and (ii) solid product obtained from crystallization of **H₂L** from a precipitated compound from solvents other than the one where suitable crystals were obtained.

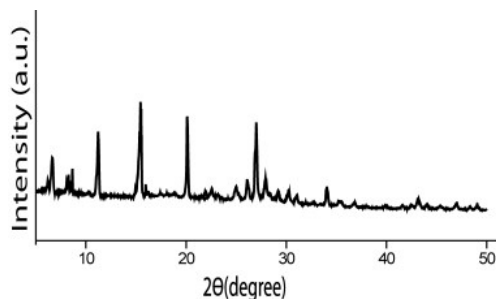


Figure S9: Powder X-ray diffraction pattern of solid product obtained from crystallization of **H₂L₁** from a precipitated compound from solvents other than the one where suitable crystals were obtained.

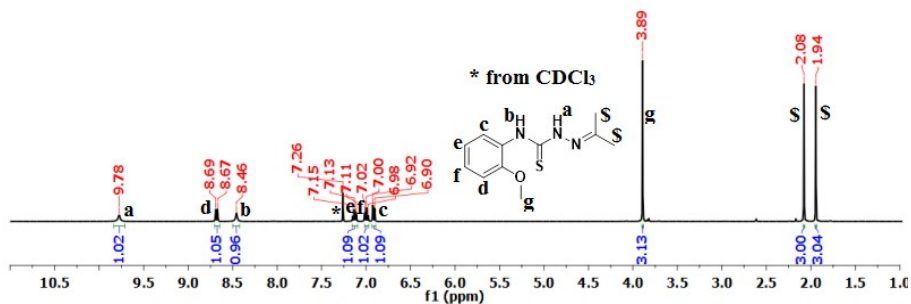


Figure S10: ¹H-NMR (600 MHz, CDCl₃) spectra of **H₂L**.

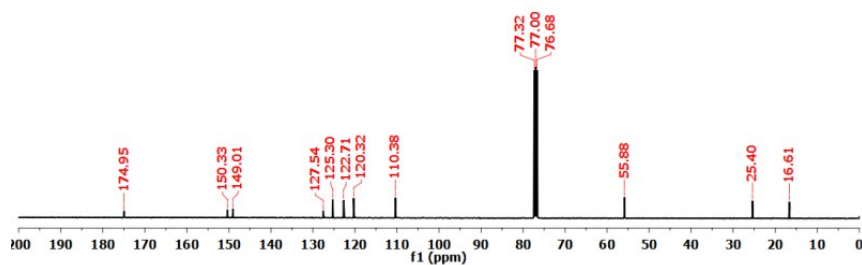


Figure S11: ¹³C-NMR (150 MHz, CDCl₃) spectra of **H₂L**.

Table S1: Different torsion angles of polymorph **Methoxypoly1** and **Methoxypoly2**.

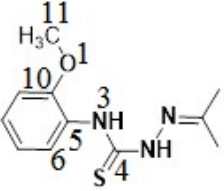
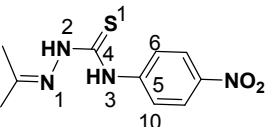
Compound H₂L	Torsion angle (°)	Methoxypoly1	Methoxypoly2
	C6-C5-N3-C4	-77.8(3)	-61.9(4)
	N2-C4-N3-C5	-178.2(2)	-176.5(2)
	S1-C4-N3-C5	2.0(3)	1.7(4)
	C5-C10-O1-C11	-174.7(2)	177.4(3)

Table S2: Different torsion angles of polymorph **Nitropoly1**, **Nitropoly2** and **Nitropoly3**.

compound H₂L₁	Torsion angle (°)	Nitropoly1 [#]	Nitropoly2	Nitropoly3
	S1-C4-N2-N1	-179.9(2)/175.5(2)	-177.0(2)	179.1(5)
	S1-C4-N3-C5	-5.9(5)/180.0(3)	-0.2(4)	1.0(1)
	C6-C5-N3-C4	1.1(5)/5.1(5)	-3.4(4)	9.0(1)
	C10-C5-N3-C4	-177.7(3)/-175.2(3)	176.2(2)	-171.5(6)

Torsion angles are from CCDC recode SEWYIF but numberings here are as per the figure given in the first column.

Table S3: Relative contributions from various interactions from Hirshfeld analysis of different polymorphs of **H₂L** and **H₂L₁**.

	Methoxypoly1	Nitropoly2	Nitropoly1	Nitropoly2	Nitropoly3
O...O	0.0	0.0	0.0	0.0	0.0
N...O	0.0	0.0	1.0	0.4	0.0
C...O	0.1	0.4	2.0	4.2	4.0
H...O	5.7	5.4	23.4	22.4	23.2
S...H	17.0	14.7	13.7	15.1	13.7
C...N	0.1	1.1	5.2	4.5	4.9
N...H	5.8	6.2	3.4	3.2	5.9
C...H	13.8	17.0	7.6	9.6	7.6
C...C	2.0	0.8	4.4	2.2	3.3
H...H	54.8	53.8	36.8	35.9	35.9

DFT calculation details:

Gaussian 09 was used for all calculations. Optimization was done by DFT using B3LYP/6-31+G(d,p) as basis set.

Table S4: XYZ coordinates of self-assembly of polymorph **Methoxypoly1**.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	-1.686311	-1.359705	0.146722
2	6	-2.615480	0.053671	0.124402
3	6	-5.005031	-0.789795	0.080141
4	6	-6.307871	-0.241964	-0.058029
5	6	-2.159406	3.572832	0.137497
6	6	-7.426593	-1.069677	-0.077424
7	1	-8.418518	-0.645787	-0.184449
8	6	-4.870109	-2.174965	0.201786
9	1	-3.881579	-2.597190	0.310732
10	6	-7.270845	-2.455232	0.040900
11	1	-8.148619	-3.094996	0.023729
12	6	-3.069377	4.767737	0.043372
13	1	-4.108664	4.452541	-0.073101
14	1	-2.791486	5.400851	-0.810170
15	1	-2.983115	5.393079	0.942152
16	6	-0.679897	3.818794	0.285641
17	1	-0.242219	3.203978	1.080194
18	1	-0.484095	4.869017	0.518014
19	1	-0.141617	3.575010	-0.639360
20	6	-5.999511	-2.998886	0.180141
21	1	-5.869916	-4.073136	0.274944
22	6	-7.615765	1.755610	-0.290168
23	1	-8.135270	1.429940	-1.200487
24	1	-7.411904	2.825950	-0.352742
25	1	-8.252089	1.555485	0.581494
26	8	-6.351885	1.125304	-0.163120
27	7	-1.977114	1.272820	0.140975
28	1	-0.953620	1.257830	0.107976
29	7	-3.964590	0.155872	0.095306
30	1	-4.284275	1.123922	0.050887
31	7	-2.722793	2.418365	0.076845
32	16	1.686268	1.359725	-0.146639
33	6	2.615441	-0.053648	-0.124305
34	6	5.005008	0.789808	-0.080236
35	6	6.307852	0.241953	0.057800
36	6	2.159465	-3.572828	-0.137186
37	6	7.426592	1.069643	0.077088
38	1	8.418520	0.645732	0.184010
39	6	4.870102	2.174983	-0.201854
40	1	3.881570	2.597229	-0.310696
41	6	7.270860	2.455201	-0.041212
42	1	8.148648	3.094947	-0.024126
43	6	3.069509	-4.767686	-0.043174
44	1	4.108801	-4.452435	0.073107
45	1	2.791795	-5.400777	0.810442
46	1	2.983123	-5.393069	-0.941913
47	6	0.679945	-3.818863	-0.285103
48	1	0.242176	-3.204277	-1.079785
49	1	0.484135	-4.869152	-0.517166
50	1	0.141758	-3.574822	0.639884
51	6	5.999523	2.998881	-0.180318
52	1	5.869939	4.073134	-0.275100

53	6	7.615729	-1.755647	0.289806
54	1	8.135330	-1.429987	1.200074
55	1	7.411853	-2.825983	0.352400
56	1	8.251972	-1.555535	-0.581918
57	8	6.351849	-1.125316	0.162881
58	7	1.977089	-1.272807	-0.140757
59	1	0.953591	-1.257845	-0.107770
60	7	3.964554	-0.155846	-0.095292
61	1	4.284237	-1.123897	-0.050874
62	7	2.722807	-2.418331	-0.076676

Table S5: XYZ coordinates of self-assembly of polymorph **Methoxypoly2**.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	1.657162	-1.393748	0.525606
2	6	2.141366	3.534266	0.630282
3	6	4.883709	-0.803911	-0.252472
4	6	2.562704	0.024376	0.341178
5	6	6.144965	-0.241941	-0.584462
6	6	4.757333	-2.194730	-0.220331
7	1	3.800278	-2.627535	0.032792
8	6	7.231753	-1.061161	-0.875031
9	1	8.191763	-0.626119	-1.128388
10	6	2.994694	4.741597	0.347855
11	1	3.168867	5.317806	1.266425
12	1	2.490865	5.415860	-0.357873
13	1	3.956505	4.442773	-0.074790
14	6	0.765862	3.765651	1.200623
15	1	0.002738	3.753528	0.411634
16	1	0.716438	4.742716	1.690488
17	1	0.487612	2.998460	1.930403
18	6	5.854862	-3.010101	-0.512952
19	1	5.732869	-4.088951	-0.481963
20	6	7.085183	-2.452371	-0.839232
21	1	7.937924	-3.085498	-1.067287
22	6	7.404721	1.773593	-0.911119
23	1	8.196161	1.511007	-0.197416
24	1	7.203586	2.844628	-0.851645
25	1	7.733961	1.520340	-1.927026
26	8	6.183356	1.129561	-0.588256
27	7	1.948789	1.237078	0.553657
28	1	0.931190	1.221108	0.672805
29	7	3.872688	0.134152	0.020993
30	1	4.179460	1.104864	-0.050353
31	7	2.659670	2.390784	0.350712
32	16	-1.657280	1.393893	0.525851
33	6	-2.141283	-3.534132	0.630460
34	6	-4.883767	0.803879	-0.252399
35	6	-2.562729	-0.024282	0.341331
36	6	-6.144946	0.241812	-0.584516
37	6	-4.757510	2.194708	-0.220215
38	1	-3.800504	2.627577	0.032988
39	6	-7.231787	1.060949	-0.875122
40	1	-8.191746	0.625834	-1.128549
41	6	-2.994530	-4.741521	0.348005
42	1	-2.490503	-5.415907	-0.357468
43	1	-3.168945	-5.317551	1.266628
44	1	-3.956226	-4.442778	-0.074959
45	6	-0.765830	-3.765449	1.200972
46	1	-0.487677	-2.998191	1.930704
47	1	-0.716448	-4.742481	1.690918
48	1	-0.002627	-3.753383	0.412060
49	6	-5.855088	3.009994	-0.512887
50	1	-5.733191	4.088854	-0.481872

51	6	-7.085340	2.452170	-0.839262
52	1	-7.938122	3.085236	-1.067342
53	6	-7.404472	-1.773833	-0.911378
54	1	-7.733680	-1.520512	-1.927278
55	1	-7.203216	-2.844851	-0.852011
56	1	-8.195988	-1.511415	-0.197698
57	8	-6.183207	-1.129691	-0.588372
58	7	-1.948753	-1.236951	0.553791
59	1	-0.931159	-1.220983	0.672896
60	7	-3.872698	-0.134124	0.021105
61	1	-4.179402	-1.104850	-0.050304
62	7	-2.659596	-2.390689	0.350777

Table S6: XYZ coordinates of self-assembly of polymorph **Nitropoly1**.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	-1.980248	0.860644	-0.816777
2	6	-4.841908	-0.632753	0.153867
3	6	-2.401382	-0.749809	-0.535113
4	6	-5.163347	0.715670	-0.081489
5	1	-4.422426	1.377589	-0.504457
6	6	-1.003095	-3.998229	-0.716127
7	6	-7.380343	0.324517	0.778124
8	6	-5.820513	-1.488372	0.702684
9	1	-5.577320	-2.531268	0.886443
10	6	-7.084525	-1.018153	1.015336
11	1	-7.841599	-1.665660	1.438645
12	6	-6.432228	1.187451	0.233831
13	1	-6.698330	2.222293	0.059045
14	6	0.329877	-3.854809	-1.401030
15	1	0.324554	-3.058186	-2.150111
16	1	0.604786	-4.791146	-1.892546
17	1	1.118513	-3.620264	-0.676039
18	6	-1.442130	-5.381135	-0.322069
19	1	-2.408525	-5.353765	0.183373
20	1	-0.704694	-5.841426	0.346861
21	1	-1.515689	-6.027703	-1.204841
22	7	-3.610487	-1.230839	-0.134308
23	1	-3.568712	-2.239963	0.007563
24	7	-1.472317	-1.738055	-0.726610
25	1	-0.508878	-1.435307	-0.898428
26	7	-1.808191	-3.037257	-0.425227
27	7	-8.712957	0.832048	1.106366
28	8	-9.528293	0.037987	1.580196
29	8	-8.943915	2.023020	0.890196
30	16	1.980241	-0.860643	-0.816661
31	6	4.841882	0.632749	0.153929
32	6	2.401370	0.749821	-0.535080
33	6	5.163353	-0.715639	-0.081588
34	1	4.422454	-1.377524	-0.504646
35	6	1.003149	3.998265	-0.716189
36	6	7.380325	-0.324545	0.778113
37	6	5.820460	1.488321	0.702866
38	1	5.577241	2.531189	0.886750
39	6	7.084477	1.018091	1.015481
40	1	7.841530	1.665562	1.438881
41	6	6.432238	-1.187432	0.233697
42	1	6.698365	-2.222247	0.058788
43	6	-0.329733	3.854875	-1.401274
44	1	-0.324402	3.058123	-2.150213
45	1	-0.604446	4.791166	-1.892993
46	1	-1.118513	3.620575	-0.676358
47	6	1.442076	5.381150	-0.321934
48	1	2.408396	5.353764	0.183651
49	1	0.704525	5.841354	0.346928

50	1	1.515746	6.027801	-1.204636
51	7	3.610456	1.230841	-0.134203
52	1	3.568685	2.239965	0.007675
53	7	1.472358	1.738092	-0.726739
54	1	0.508843	1.435427	-0.898277
55	7	1.808227	3.037291	-0.425244
56	7	8.712943	-0.832090	1.106318
57	8	9.528261	-0.038068	1.580243
58	8	8.943921	-2.023037	0.890026

Table S7: XYZ coordinates of self-assembly of polymorph **Nitropoly2**.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	-0.226504	1.764528	1.219564
2	6	-1.698485	1.909470	0.409782
3	6	-4.106115	4.501465	1.538719
4	1	-4.866519	4.161085	0.840231
5	6	-2.850005	3.858276	1.567189
6	6	-3.495532	0.413939	-2.257104
7	6	-3.403924	5.982975	3.282309
8	6	-4.387431	5.557704	2.388344
9	1	-5.349151	6.055057	2.372504
10	6	-2.156057	5.365600	3.327530
11	1	-1.413694	5.721599	4.031316
12	6	-2.569020	-0.593945	-2.886276
13	1	-1.553004	-0.200984	-3.001455
14	1	-2.936083	-0.889971	-3.872410
15	1	-2.498363	-1.501423	-2.272557
16	6	-4.868648	0.574363	-2.849461
17	1	-5.449765	1.314416	-2.295130
18	1	-5.406949	-0.382558	-2.836366
19	1	-4.801304	0.885298	-3.900239
20	6	-1.872531	4.305501	2.473799
21	1	-0.906314	3.824196	2.504494
22	7	-1.995312	1.058852	-0.624308
23	1	-1.321788	0.311100	-0.815365
24	7	-3.218413	1.152260	-1.240467
25	7	-2.690538	2.812153	0.651454
26	1	-3.486127	2.653409	0.032535
27	7	-3.691223	7.097573	4.185205
28	8	-4.805032	7.621210	4.113168
29	8	-2.804495	7.449254	4.965303
30	16	0.226504	-1.764528	-1.219564
31	6	1.698485	-1.909470	-0.409782
32	6	4.106115	-4.501465	-1.538719
33	1	4.866519	-4.161085	-0.840231
34	6	2.850005	-3.858276	-1.567189
35	6	3.495532	-0.413939	2.257104
36	6	3.403924	-5.982975	-3.282309
37	6	4.387431	-5.557704	-2.388344
38	1	5.349151	-6.055057	-2.372504
39	6	2.156057	-5.365600	-3.327530
40	1	1.413694	-5.721599	-4.031316
41	6	2.569020	0.593945	2.886276
42	1	1.553004	0.200984	3.001455
43	1	2.936083	0.889971	3.872410
44	1	2.498363	1.501423	2.272557
45	6	4.868648	-0.574363	2.849461
46	1	5.449765	-1.314416	2.295130
47	1	5.406949	0.382558	2.836366
48	1	4.801304	-0.885298	3.900239
49	6	1.872531	-4.305501	-2.473799
50	1	0.906314	-3.824196	-2.504494
51	7	1.995312	-1.058852	0.624308

52	1	1.321788	-0.311100	0.815365
53	7	3.218413	-1.152260	1.240467
54	7	2.690538	-2.812153	-0.651454
55	1	3.486127	-2.653409	-0.032535
56	7	3.691223	-7.097573	-4.185205
57	8	4.805032	-7.621210	-4.113168
58	8	2.804495	-7.449254	-4.965303

Table S8: XYZ coordinates of self-assembly of polymorph Nitropoly3.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	16	5.804967	2.786162	-0.023443
2	6	4.139452	2.599764	0.028993
3	6	5.199041	-1.631767	-1.157164
4	1	6.196955	-2.018656	-1.325171
5	6	3.703688	0.182565	-0.585615
6	6	5.006380	-0.300258	-0.805439
7	1	5.851978	0.363701	-0.697779
8	6	4.104507	-2.483033	-1.293406
9	6	1.350864	4.674630	0.776199
10	6	2.606768	-0.695187	-0.737972
11	1	1.598117	-0.326989	-0.561766
12	6	2.802446	-2.019252	-1.092024
13	1	1.967152	-2.696228	-1.224956
14	6	-0.142092	4.551750	0.878789
15	1	-0.467446	3.529428	0.670634
16	1	-0.633762	5.235493	0.173913
17	1	-0.483028	4.835107	1.883682
18	6	1.986200	6.018844	1.050048
19	1	2.673709	5.971822	1.905780
20	1	1.226900	6.770562	1.276876
21	1	2.560970	6.374752	0.184342
22	7	3.380603	1.492055	-0.219225
23	1	2.383152	1.676767	-0.106089
24	7	3.372553	3.693803	0.363427
25	1	3.891417	4.542826	0.563196
26	7	2.011789	3.616202	0.458971
27	7	4.316364	-3.886137	-1.640795
28	8	3.326115	-4.622518	-1.682694
29	8	5.469253	-4.259015	-1.863279
30	16	-0.993584	0.803562	-0.057196
31	6	-1.616859	-0.604545	0.621441
32	6	-5.481511	1.031613	-1.084585
33	1	-5.595450	1.934454	-1.671975
34	6	-4.104383	-0.544170	0.126169
35	6	-4.228293	0.631768	-0.633648
36	1	-3.352113	1.219697	-0.864831
37	6	-6.606033	0.267201	-0.783664
38	6	-0.340460	-3.396208	2.410939
39	6	-5.256856	-1.303941	0.415632
40	1	-5.166359	-2.214712	1.002487
41	6	-6.504629	-0.905189	-0.034586
42	1	-7.394998	-1.481337	0.183754
43	6	-0.856678	-4.682726	2.988679
44	1	-1.928935	-4.786685	2.810025
45	1	-0.336159	-5.539758	2.541932
46	1	-0.668180	-4.724501	4.069427
47	6	1.128945	-3.077556	2.556540
48	1	1.281992	-2.117250	3.067309
49	1	1.638882	-3.847910	3.138933
50	1	1.628202	-3.016670	1.580011
51	7	-2.901788	-1.052580	0.635927
52	1	-2.983019	-1.943367	1.125212
53	7	-0.754882	-1.460822	1.266340
54	1	0.218480	-1.175973	1.294739

55	7	-1.192914	-2.635644	1.816708
56	7	-7.920810	0.699936	-1.261483
57	8	-8.892839	-0.002143	-0.976861
58	8	-7.978777	1.739468	-1.919727
