SUPPLEMENTARY INFORMATION

Deciphering Divergent Ferroelectric Behaviour in Hydrogen-bonded Organic Polymorphs

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Table S1: Crystal structure and refinement details for the neutron diffraction data of 1P_T form.

Parameters	**1P_T**
Chemical Formula	$C_{22}H_{13}F_3N_2$
Formula weight	362.34
Space group	$P4_1$
Temperature (K)	100.0 (2)
***a=b, c* (Å)**	14.4058(5), 15.8555(6)
Volume (Å^3)	3290.4(3)
ρ (g cm^{-3})	1.463
Z	8
***F*(000)**	1104.0
Crystal size (mm^3)	1.2 × 1.0 × 0.5
Instrument	KOALA2 @ end of guide position on TG3-supermirror guide at OPAL reactor at ANSTO
Radiation	"white" neutron beam (integrated from λ = 0.80 - 1.60 Å) to minimum d_{space} = 0.55 Å
2θ range for data collection (^{o})	4.5 to 180
Index (h k l) ranges	-25≤ h ≤ 26, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28
Measured reflections	134826
Independent reflections	8632 [R_{int} = 6.1(5.6) for 36751 data at 4 σ]
Data/Restraints/Parameters	4735/1/721
Goodness-of-fit on F^2	0.805
Final *R* indices [*I*>=2σ (*I*)]	R_1 = 0.0623, wR_2 = 0.0261
Final *R* indices [all data]	R_1 = 0.0505, wR_2 = 0.0246

Table S2: Comparison of N-H bond lengths and N-H…N distances (in Å) obtained from reported average neutron distances, HAR model, and Neutron diffraction data for 1P_T (first row) and 1P_O (second row) form, respectively.

Method	Neutron Experiment	Average Neutron	HAR
N1A-H1A	1.034 (3)	1.030	0.977
	1.034 (3)	1.030	1.018
N1B-H1B	1.039 (3)	1.030	0.984
	1.039 (3)	1.030	1.005
N1A-H1A…N2B	1.852 (3)	1.856	1.906
	1.785 (3)	1.789	1.799
N1B-H1B…N2A	1.899 (3)	1.909	1.955
	1.946 (3)	1.955	1.974

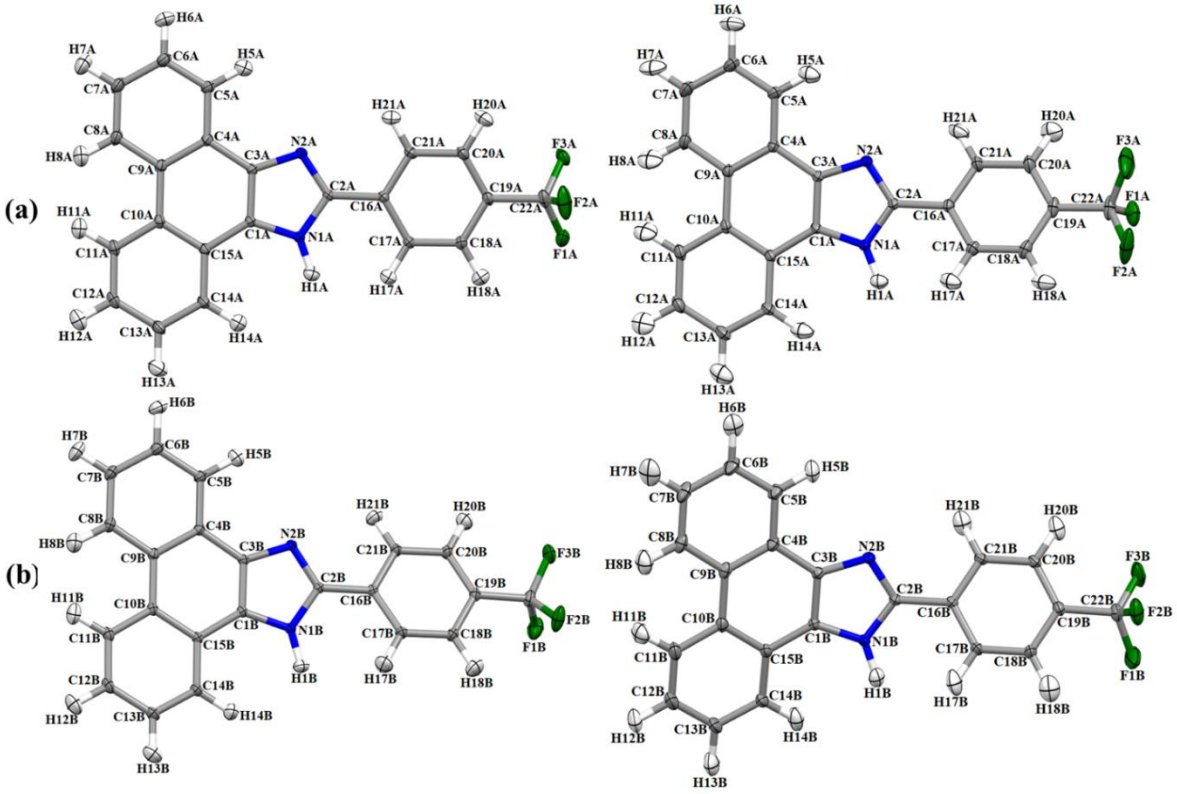

Figure S1: The ORTEP diagram is drawn at 50% ellipsoid probability for all atoms for (a) molecule A and (b) molecule B for 1P_T (left) and 1P_O (right) form.

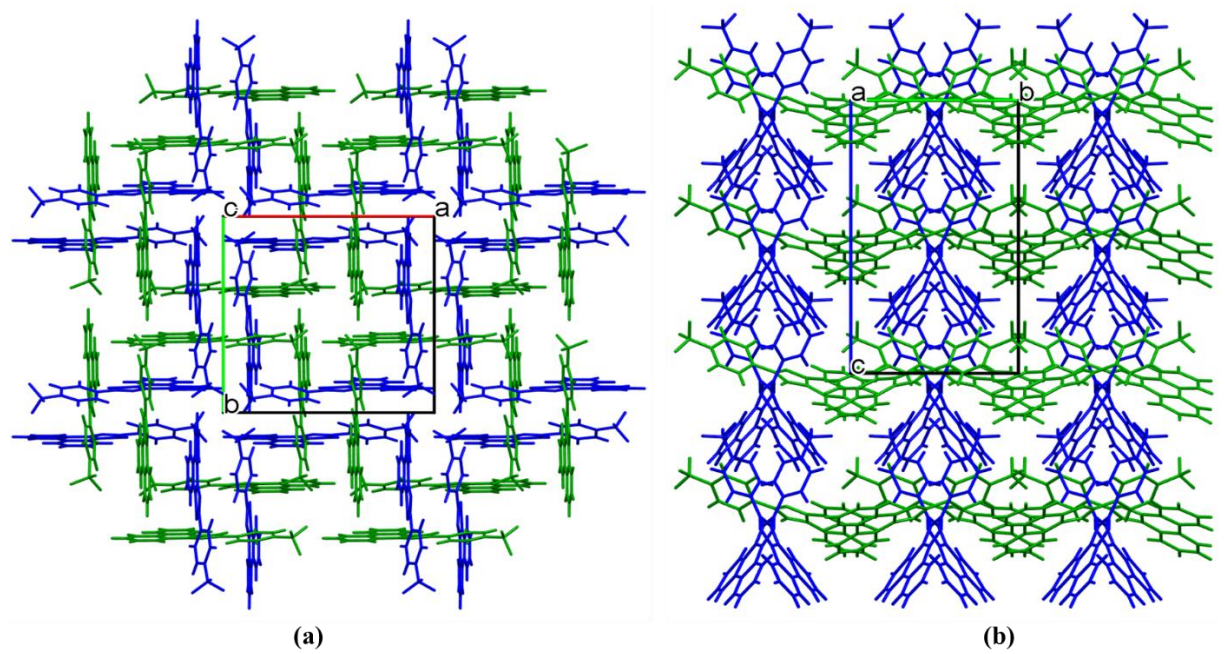

Figure S2: Molecular packing diagrams highlighting the butterfly-like arrangements in (A) 1P_T viewed down the *c*-axis and (B) 1P_O viewed down the *a*-axis.

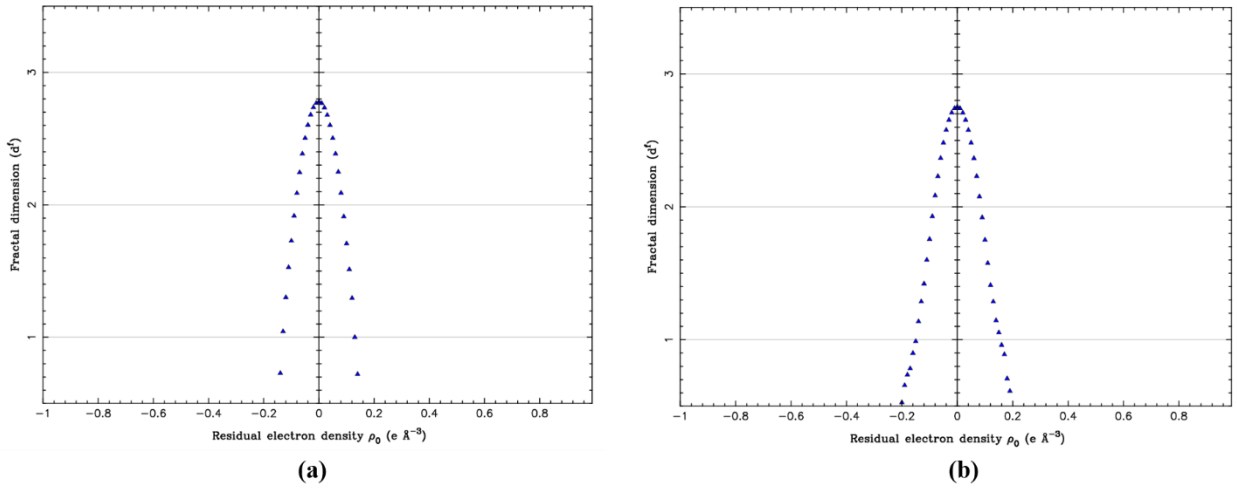

Figure S3: Fractal dimension plot based on experimental structure factor for (a) 1P_T and (b) 1P_O form.

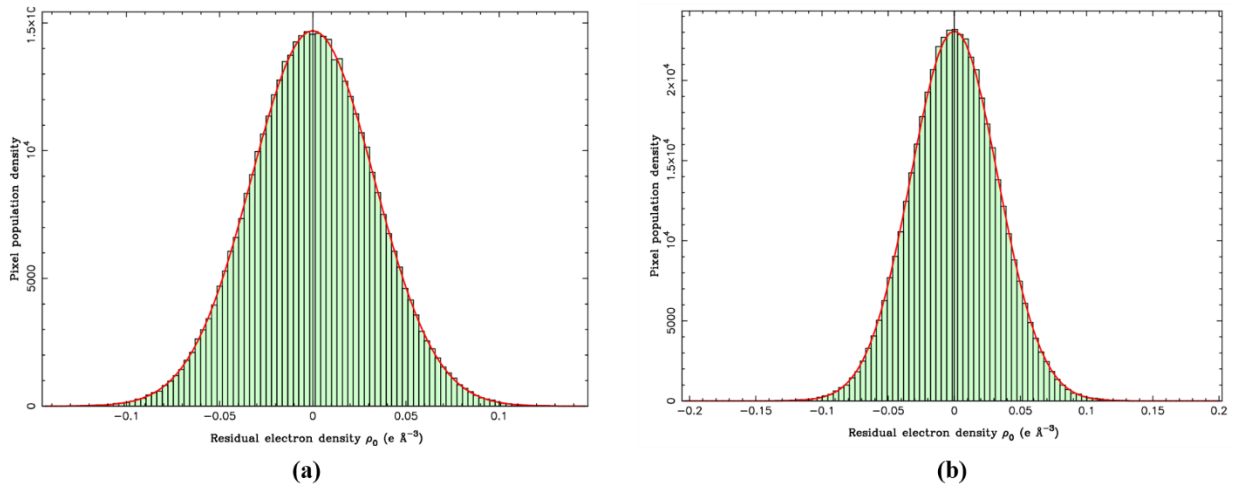

Figure S4: Residual electron density distribution plot based on experimental structure factor for (a) 1P_T and (b) 1P_O form.

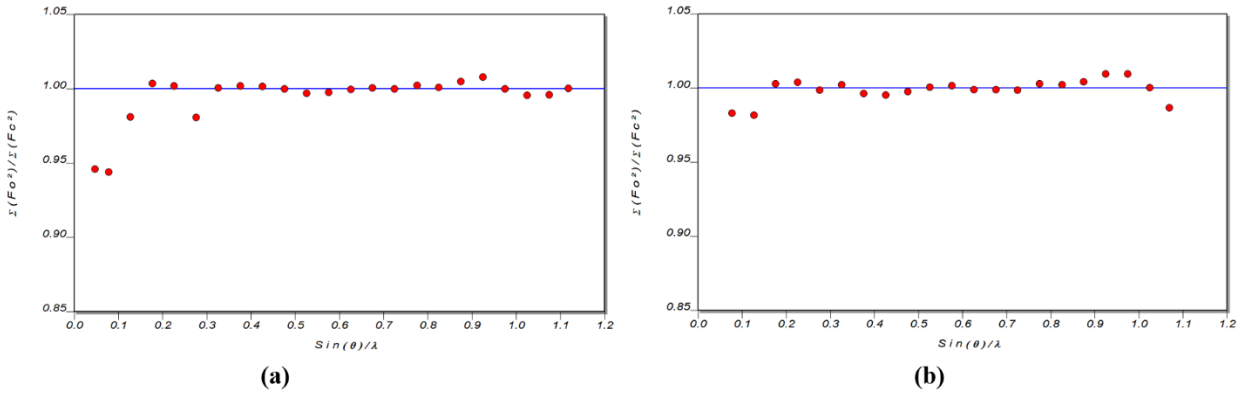

Figure S5: Scale factor vs resolution plot based on experimental structure factor for (a) 1P_T and (b) 1P_O form.

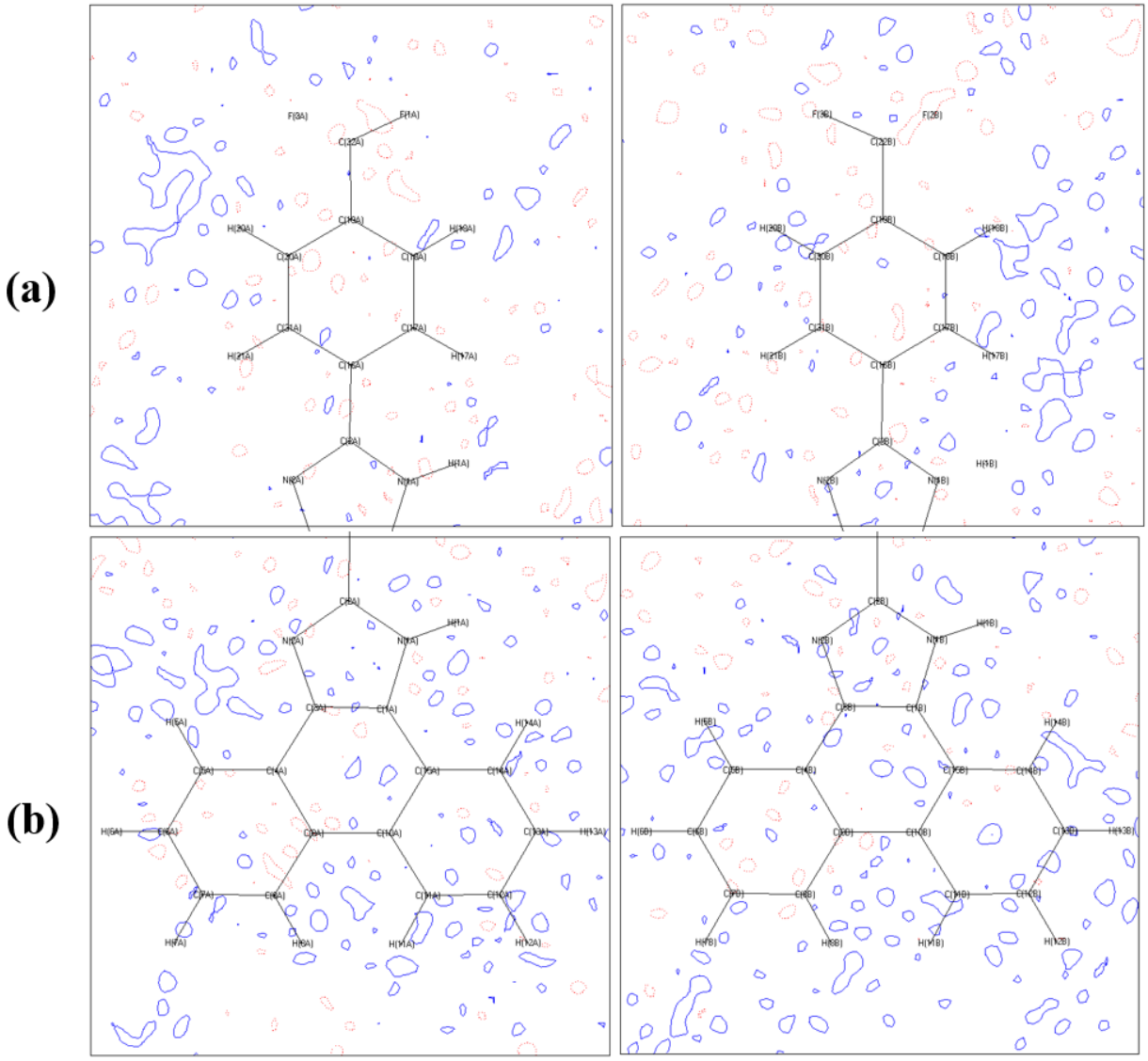

Figure S6: Experimental residual density map of 1P_T for molecule A (left) and molecule B (right) drawn in the plane containing atoms (a) C21, C17, C22, and (b) C7, C12, C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 *e* Å^{-3} with an interval of 0.1 *e* Å^{-3}.

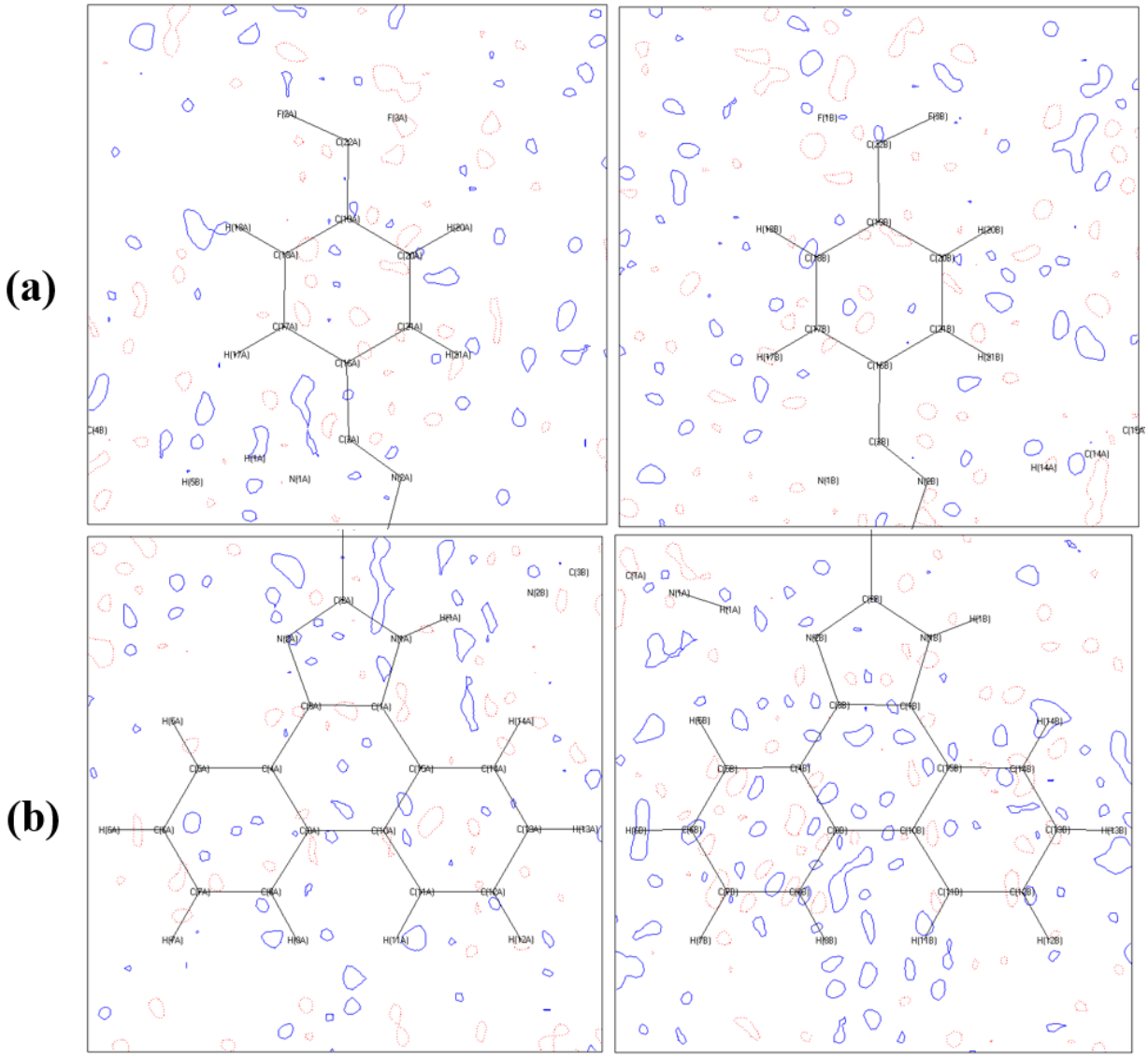

Figure S7: Experimental residual density map of 1P_O for molecule A (left) and molecule B (right) drawn in the plane containing atoms (a) C21, C17, C22, and (b) C7, C12, C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 *e* Å^{-3} with an interval of 0.1 *e* Å^{-3}.

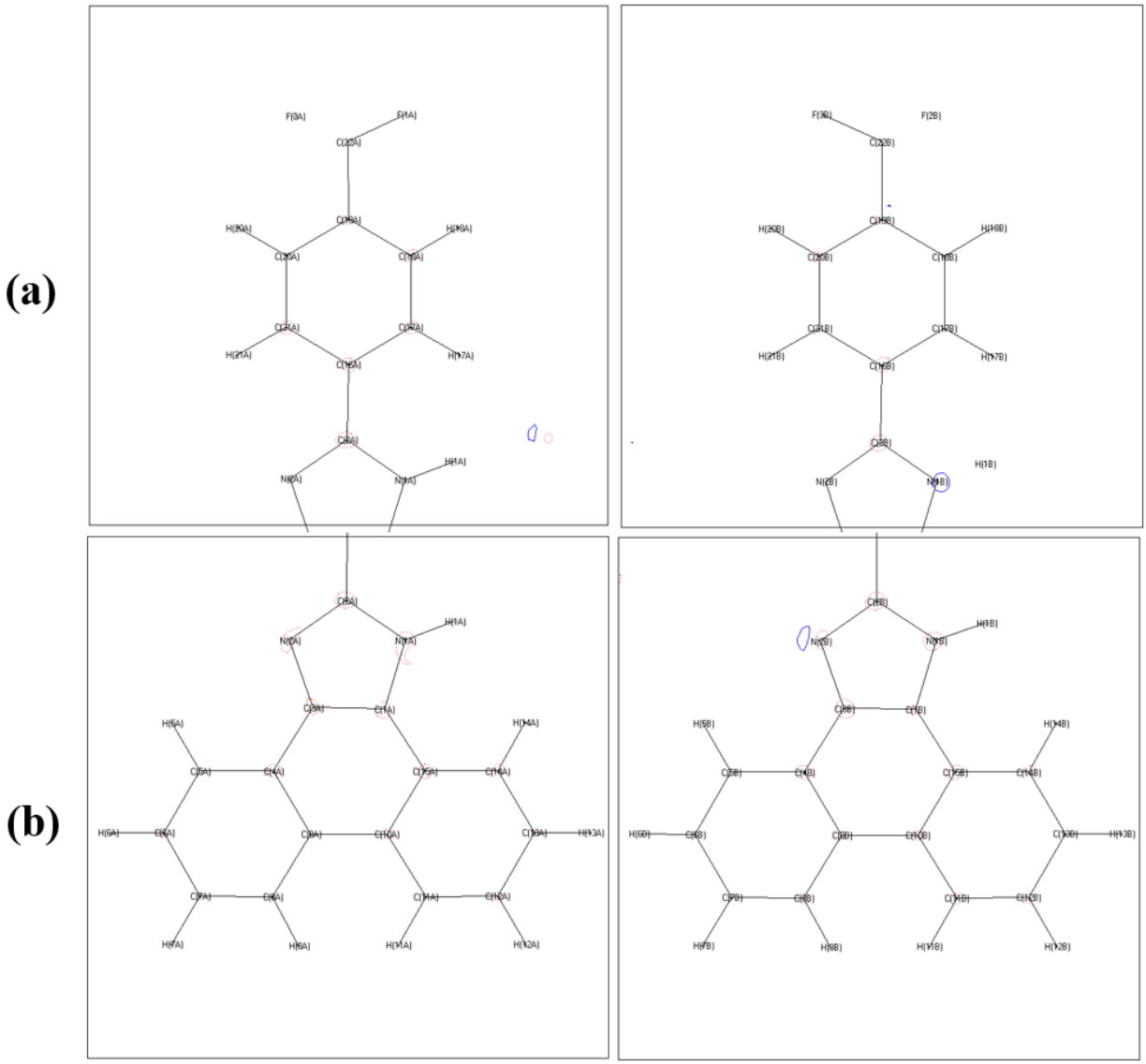

Figure S8: Theoretical residual density map of 1P_T for molecule A (left) and molecule B (right) drawn in the plane containing atoms (a) C21, C17, C22, and (b) C7, C12, C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 *e* Å^{-3} with an interval of 0.1 *e* Å^{-3}.

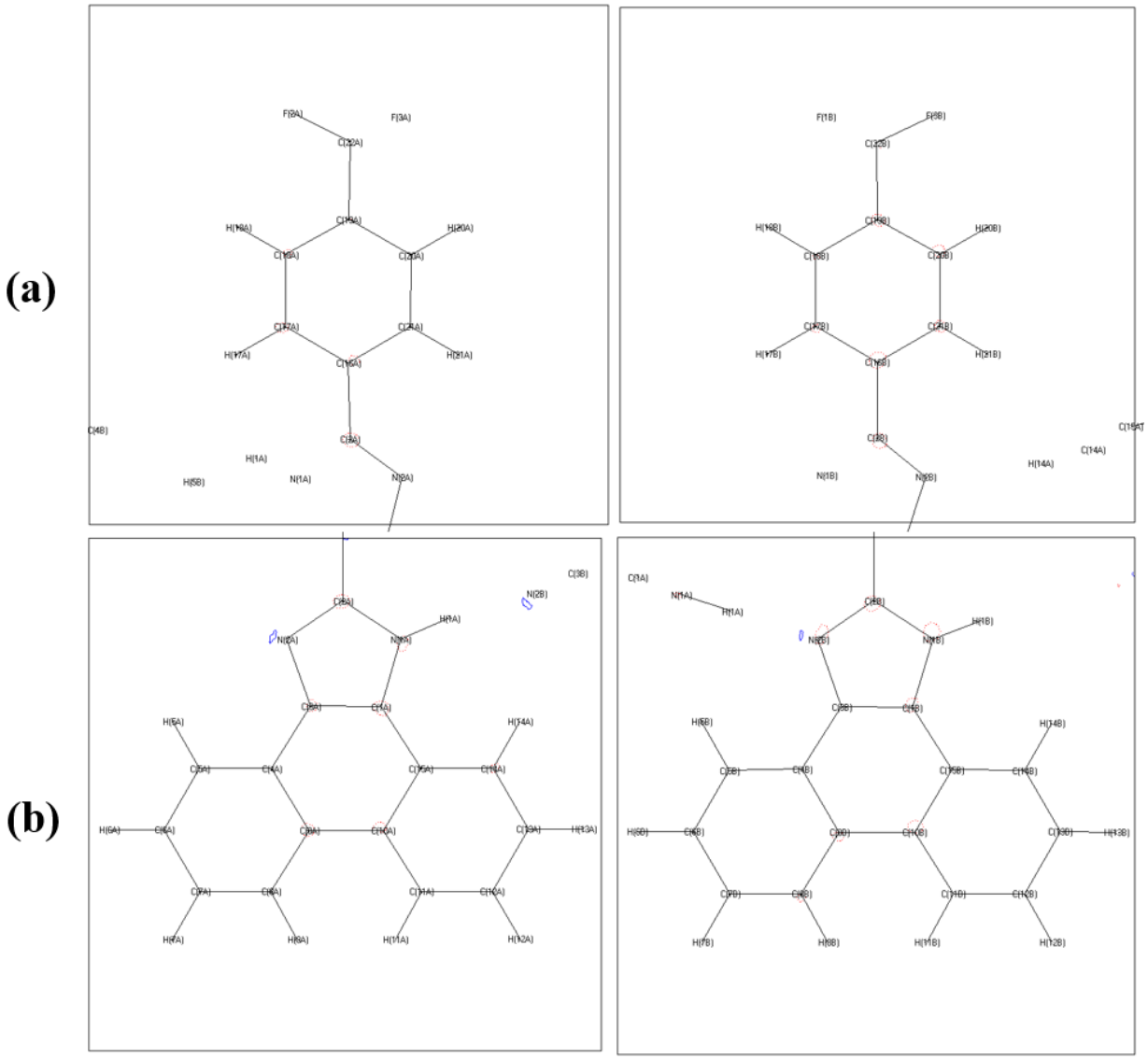

Figure S9: Theoretical residual density map of 1P_O for molecule A (left) and molecule B (right) drawn in the plane containing atoms (a) C21, C17, C22, and (b) C7, C12, C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 *e* Å^{-3} with an interval of 0.1 *e* Å^{-3}.

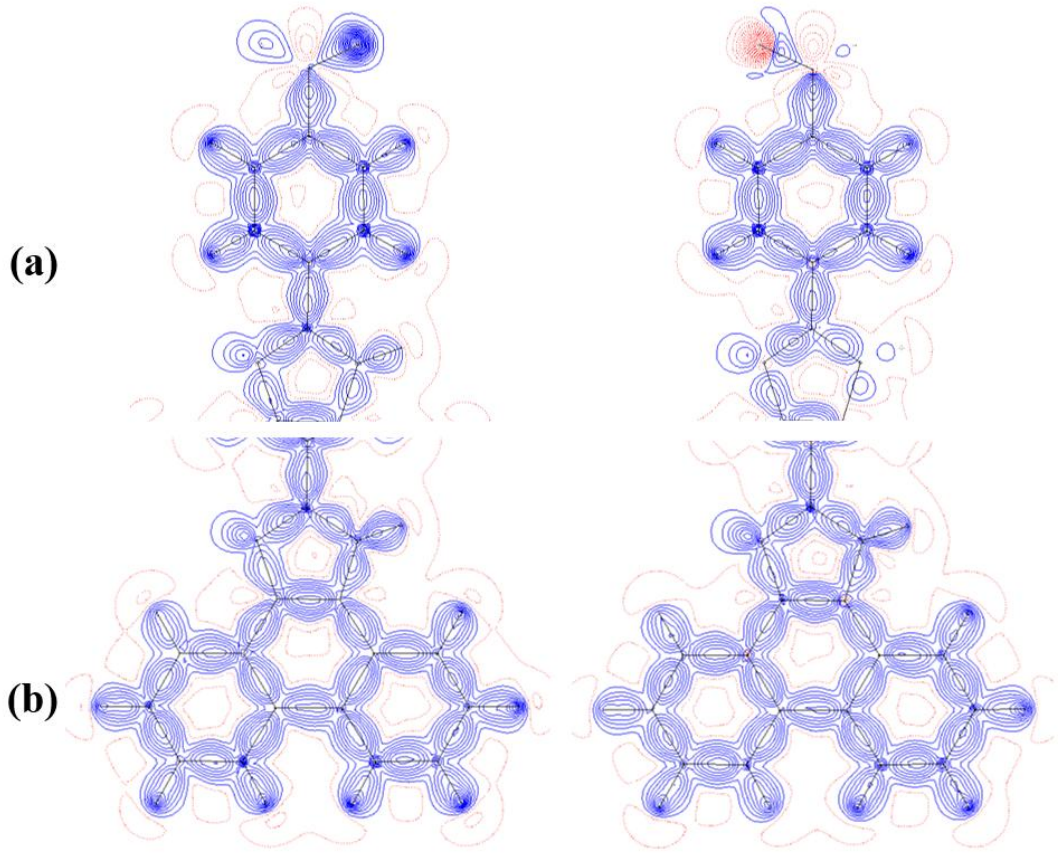

Figure S10: Experimental 2D deformation electron density map of 1P_T for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C21, C17, and C22, and (b) C7, C12, and C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 eÅ^{-3} with an interval of 0.1 eÅ^{-3}.

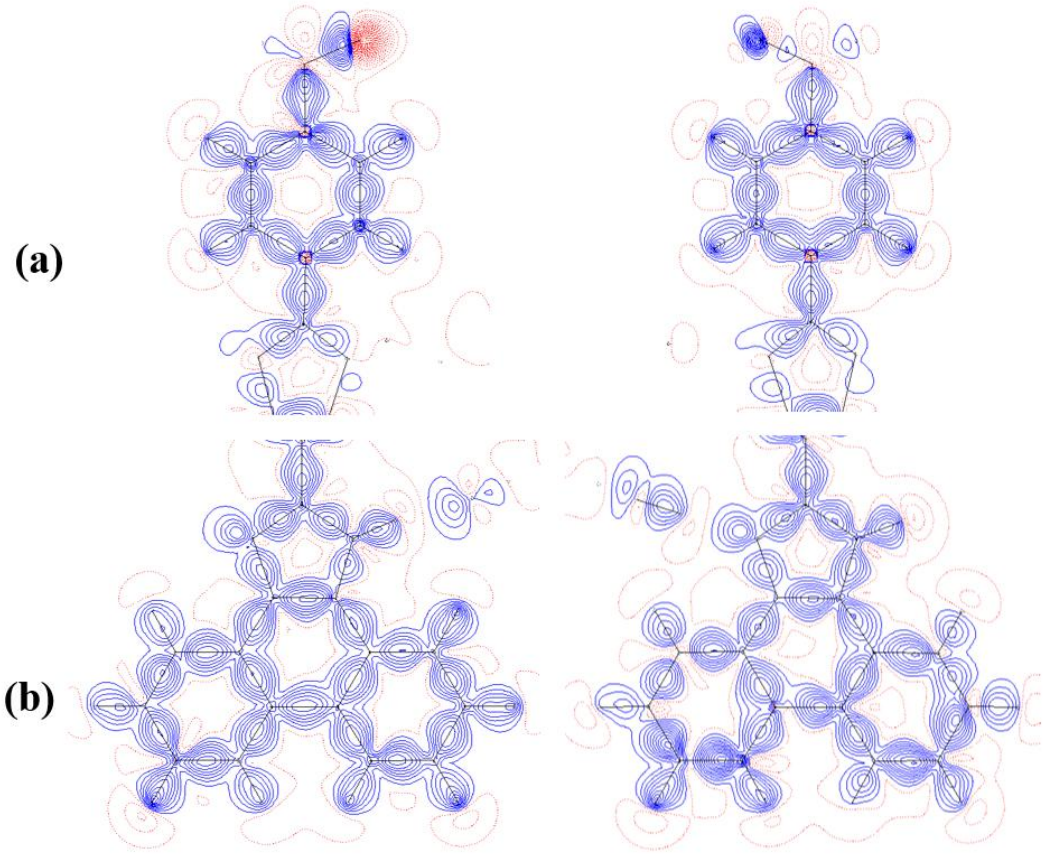

Figure S11: Experimental 2D deformation electron density map of 1P_O for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C21, C17, and C22, and (b) C7, C12, and C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 eÅ^{-3} with an interval of 0.1 eÅ^{-3}.

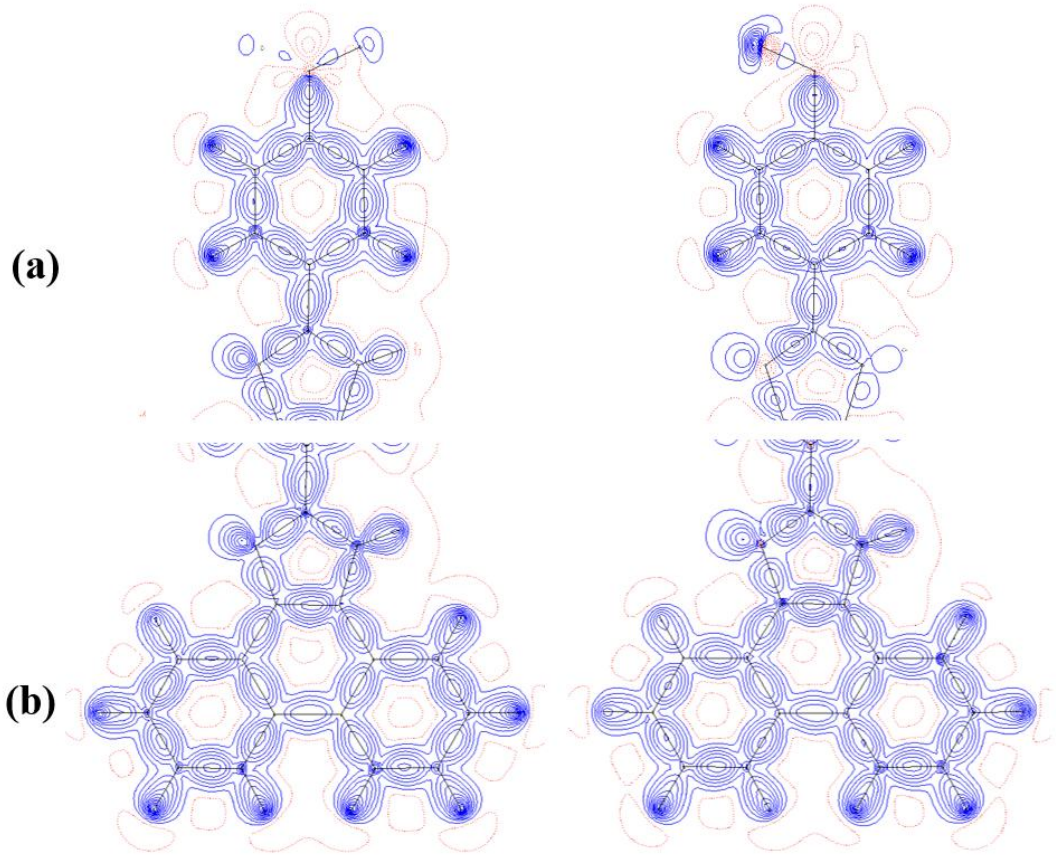

Figure S12: Theoretical 2D deformation electron density map of 1P_T for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C21, C17, and C22, and (b) C7, C12, and C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 eÅ^{-3} with an interval of 0.1 eÅ^{-3}.

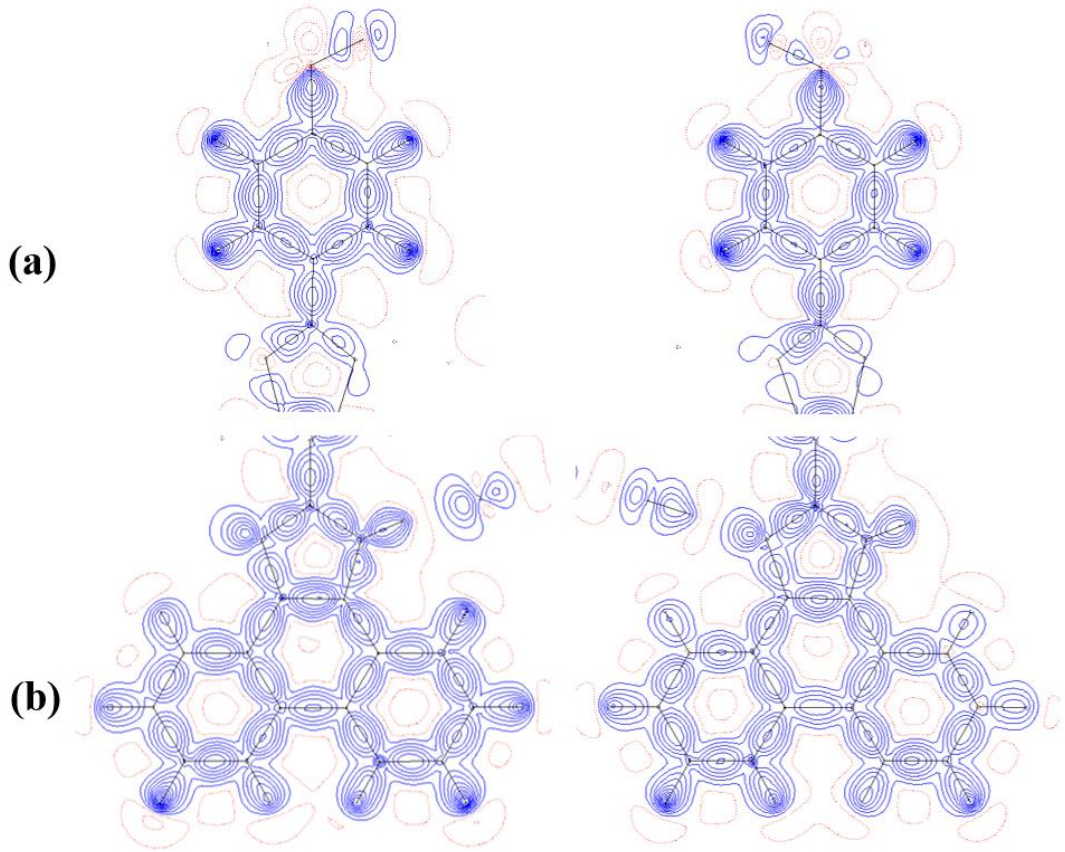

Figure S13: Theoretical 2D deformation electron density map of 1P_O for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C21, C17, and C22, and (b) C7, C12, and C2. The positive (solid blue lines) and negative (dashed red lines) contours are drawn starting from ±0.05 eÅ^{-3} with an interval of 0.1 eÅ^{-3}.

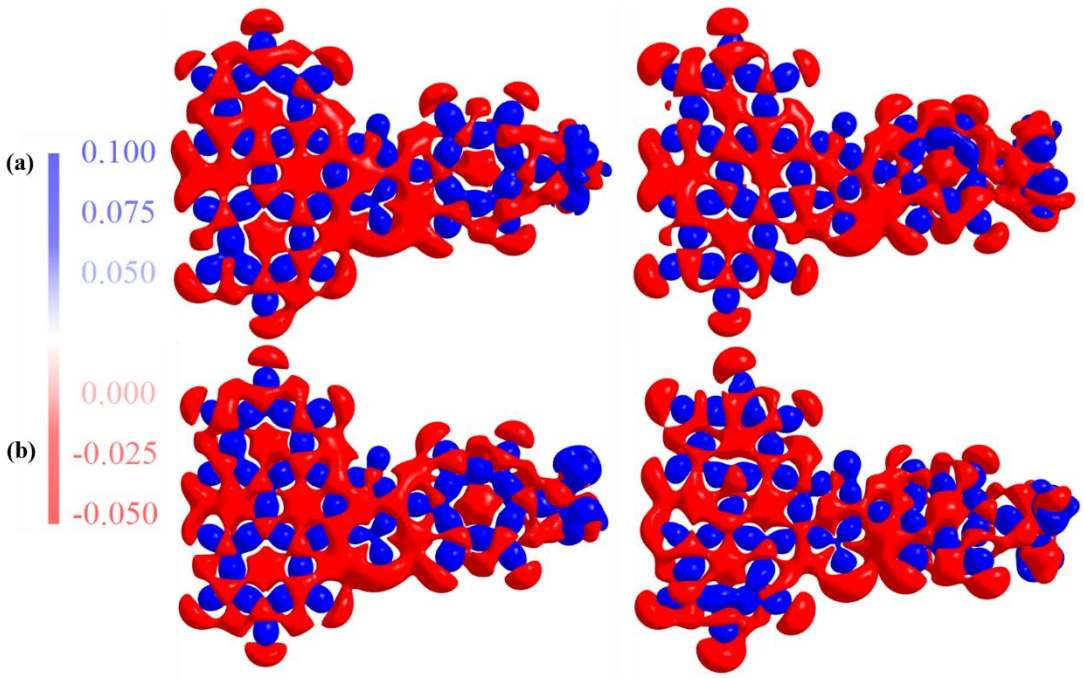

Figure S14: Experimental 3D-deformation density maps for (a) molecule A and (b) molecule B of 1P_T (left) and 1P_O (right).

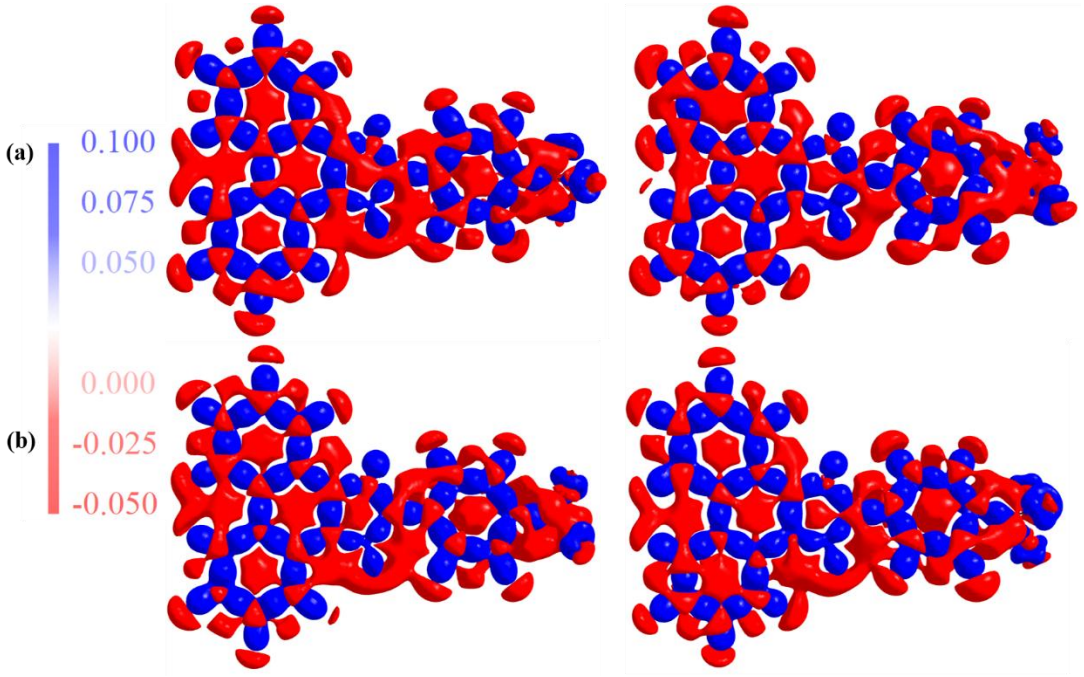

Figure S15: Theoretical 3D-deformation density maps for (a) molecule A and (b) molecule B of 1P_T (left) and 1P_O (right).

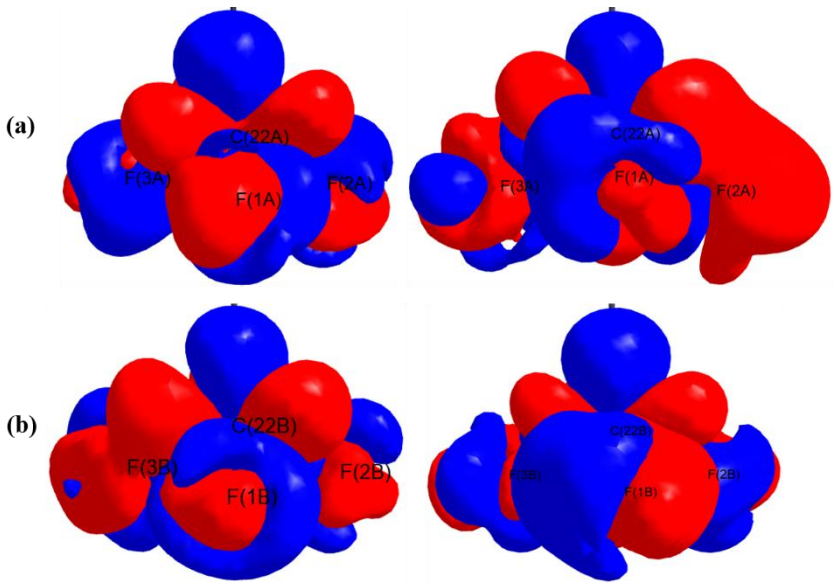

Figure S16: Experimental 3D-deformation density maps for –CF_3 group of (a) molecule A and (b) molecule B of 1P_T (left) and 1P_O (right).

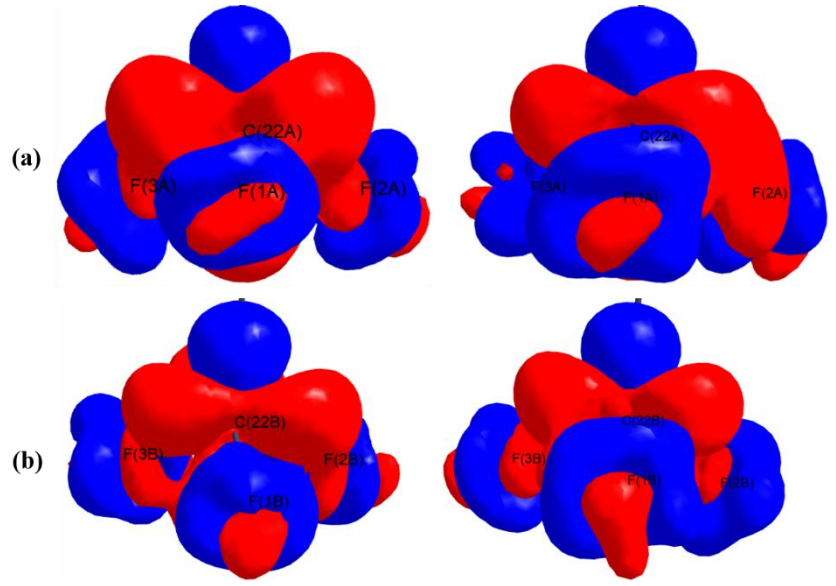

Figure S17: Theoretical 3D-deformation density maps for –CF_3 group of (a) molecule A and (b) molecule B of 1P_T (left) and 1P_O (right).

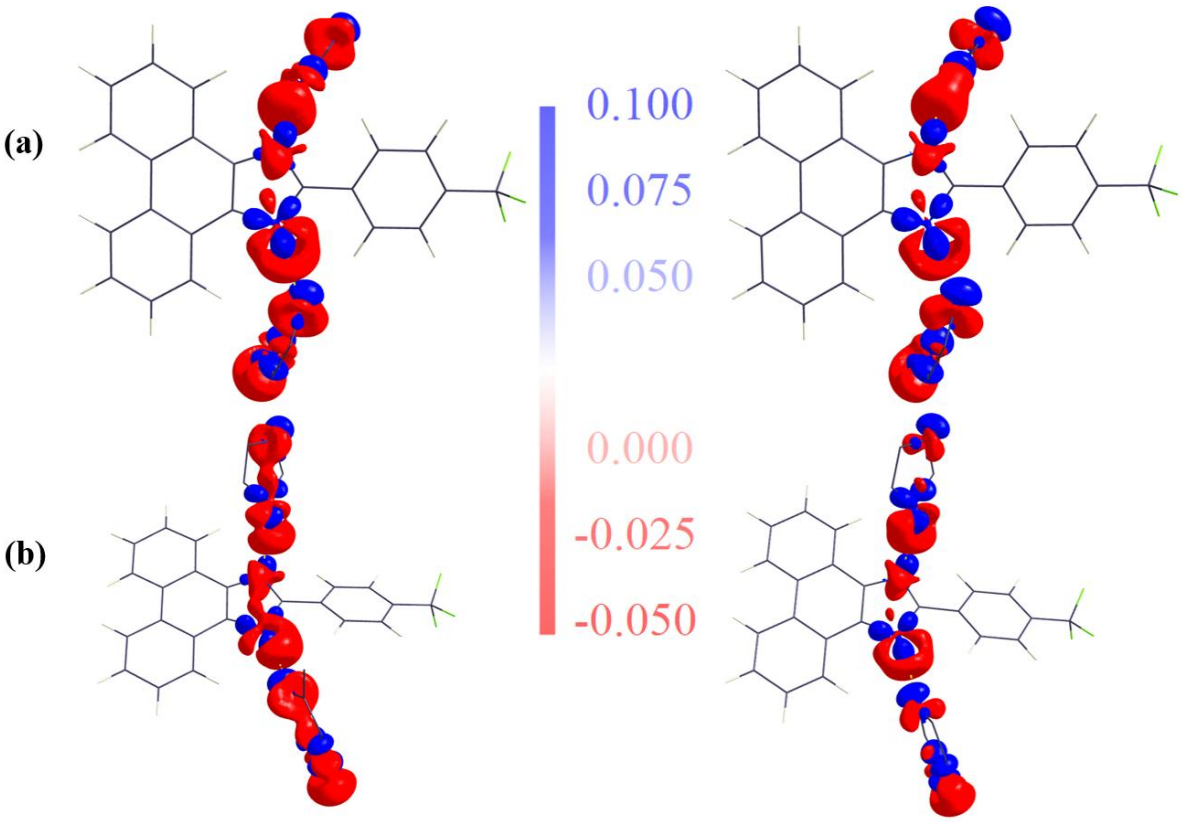

Figure S18: Experimental (left) and theoretical (right) 3D-deformation density maps, highlighting the electron density along the proton tautomeric pathway for (a) 1P_T and (b) 1P_O.

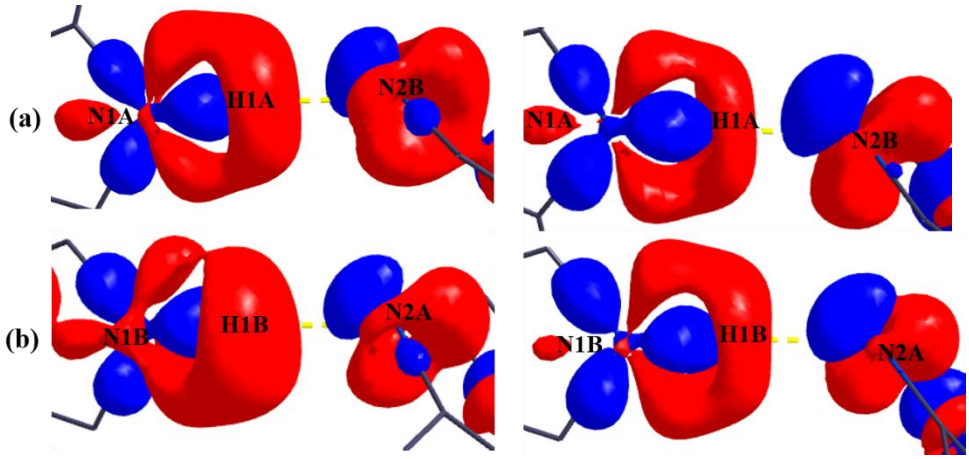

Figure S19: Experimental (left) and theoretical (right) 2D-deformation density maps for 1P_T, highlighting the electron density distribution in (a) N1A-H1A…N2B and (b) N1B-H1B…N2A hydrogen bonding region.

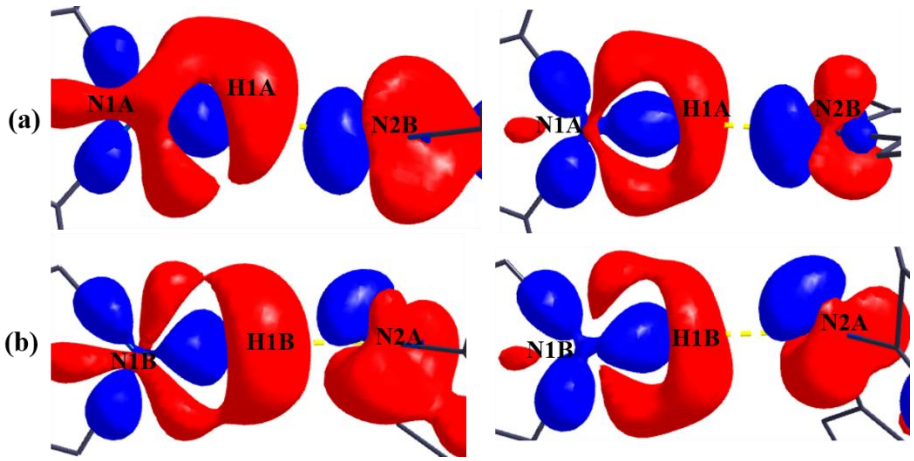

Figure S20: Experimental (left) and theoretical (right) 2D-deformation density maps for 1P_O, highlighting the electron density distribution in (a) N1A-H1A…N2B and (b) N1B-H1B…N2A hydrogen bonding region.

Table S3: Experimental (values in the first rows) and theoretical (values in italics in the second rows) topological parameters for the covalent bonds of 1P_T and those of 1P_O are listed in the third and fourth rows, respectively.

Bond	ρ	$\nabla^2\rho$	R_{ij}	λ_1	λ_2	λ_3	ε
	$(e\text{Å}^{-3})$	$(e\text{Å}^{-5})$	Å				
F(1A)-C(22A)	1.966(21)	-16.377(105)	1.374	-15.46	-14.02	13.10	0.10
	1.906(7)	*-14.29(34)*	*1.358*	*-15.52*	*-14.71*	*15.94*	*0.06*
	2.174(46)	-20.722(211)	1.334	-18.93	-17.67	15.88	0.07
	2.038(8)	*-19.69(42)*	*1.331*	*-16.61*	*-16.05*	*12.96*	*0.03*
F(2A)-C(22A)	1.939(19)	-10.449(106)	1.349	-14.65	-12.33	16.53	0.19
	1.949(7)	*-15.984(33)*	*1.344*	*-15.43*	*-15.25*	*14.70*	*0.01*
	1.989(50)	-15.201(271)	1.349	-17.87	-17.27	19.94	0.03
	1.956(8)	*-14.938(51)*	*1.325*	*-15.99*	*-14.28*	*15.33*	*0.12*
F(3A)-C(22A)	2.087(19)	-20.816(105)	1.344	-16.85	-15.63	11.67	0.08
	1.969(7)	*-17.454(37)*	*1.345*	*-16.08*	*-15.49*	*14.12*	*0.04*
	1.875(47)	-11.011(213)	1.361	-15.13	-11.71	15.83	0.29
	1.745(8)	*-9.741(41)*	*1.361*	*-12.50*	*-11.24*	*14.00*	*0.11*

N(1A)-C(1A)	2.105(15)	-19.255(68)	1.375	-16.52	-14.19	11.46	0.16
	2.052(4)	*-15.351(15)*	*1.374*	*-14.57*	*-12.86*	*12.08*	*0.13*
	1.960(31)	-17.232(148)	1.377	-13.62	-12.99	9.38	0.05
	2.034(4)	*-15.228(16)*	*1.379*	*-14.40*	*-12.51*	*11.68*	*0.15*
N(1A)-C(2A)	2.201(14)	-21.181(65)	1.366	-18.40	-14.30	11.52	0.29
	2.129(4)	*-18.27(17)*	*1.367*	*-16.26*	*-13.46*	*11.45*	*0.21*
	2.195(25)	-23.753(109)	1.363	-17.78	-13.70	7.73	0.30
	2.147(2)	*-19.192(11)*	*1.364*	*-15.29*	*-13.47*	*9.56*	*0.14*
N(2A)-C(2A)	2.491(21)	-23.416(82)	1.334	-20.46	-17.65	14.69	0.16
	2.361(5)	*-20.973(21)*	*1.334*	*-17.91*	*-15.96*	*12.90*	*0.12*
	2.451(32)	-25.126(122)	1.334	-19.89	-16.77	11.53	0.19
	2.325(3)	*-20.758(13)*	*1.334*	*-17.12*	*-15.02*	*11.38*	*0.14*
N(2A)-C(3A)	2.132(18)	-15.58(69)	1.381	-16.71	-14.85	15.98	0.13
	2.114(4)	*-14.284(13)*	*1.381*	*-15.19*	*-13.87*	*14.77*	*0.09*
	2.164(33)	-17.972(128)	1.383	-16.98	-14.94	13.95	0.14
	2.076(3)	*-13.231(10)*	*1.382*	*-14.71*	*-13.35*	*14.83*	*0.10*
C(1A)-C(3A)	2.232(18)	-20.98(54)	1.385	-17.78	-13.91	10.72	0.28
	2.134(4)	*-17.674(12)*	*1.385*	*-15.52*	*-12.44*	*10.29*	*0.25*
	2.195(36)	-19.504(101)	1.385	-17.03	-13.47	10.99	0.26
	2.158(4)	*-18.485(12)*	*1.385*	*-15.84*	*-13.04*	*10.39*	*0.21*
C(1A)-C(15A)	2.026(15)	-17.005(43)	1.429	-15.81	-12.74	11.54	0.24
	1.932(3)	*-14.502(10)*	*1.429*	*-13.68*	*-11.81*	*10.99*	*0.16*
	1.975(30)	-15.459(76)	1.431	-14.49	-12.32	11.35	0.18
	1.947(3)	*-14.768(8)*	*1.430*	*-13.80*	*-12.02*	*11.06*	*0.15*
C(2A)-C(16A)	1.882(20)	-14.097(58)	1.465	-14.82	-11.88	12.61	0.25
	1.833(3)	*-12.631(9)*	*1.465*	*-12.82*	*-11.06*	*11.24*	*0.16*
	1.862(31)	-14.772(87)	1.466	-14.30	-11.66	11.18	0.23
	1.807(2)	*-12.401(6)*	*1.466*	*-12.29*	*-10.52*	*10.41*	*0.17*
	1.982(15)	-17.033(44)	1.435	-15.84	-12.85	11.66	0.23
	1.929(3)	*-14.688(8)*	*1.435*	*-13.69*	*-11.60*	*10.60*	*0.18*

C(3A)-C(4A)	2.006(27)	-17.513(68)	1.434	-15.36	-12.55	10.40	0.22
	1.904(3)	*-14.122(8)*	*1.434*	*-13.42*	*-11.53*	*10.83*	*0.16*
C(4A)-C(5A)	2.067(13)	-17.449(33)	1.408	-15.50	-13.13	11.18	0.18
	2.038(3)	*-16.347(7)*	*1.408*	*-14.38*	*-12.27*	*10.31*	*0.17*
	2.095(24)	-18.335(55)	1.409	-15.71	-12.81	10.18	0.23
	2.020(2)	*-15.58(6)*	*1.409*	*-13.86*	*-12.12*	*10.40*	*0.14*
C(4A)-C(9A)	2.058(16)	-17.285(44)	1.421	-16.05	-13.38	12.15	0.20
	1.973(3)	*-15.095(8)*	*1.421*	*-13.68*	*-12.16*	*10.75*	*0.12*
	2.066(24)	-18.342(59)	1.421	-15.32	-13.09	10.07	0.17
	1.956(3)	*-14.494(8)*	*1.420*	*-13.69*	*-11.75*	*10.94*	*0.17*
C(5A)-C(6A)	2.189(12)	-19.872(32)	1.380	-16.70	-13.17	10.00	0.27
	2.190(2)	*-19.457(7)*	*1.380*	*-15.68*	*-13.17*	*9.39*	*0.19*
	2.202(27)	-21.292(72)	1.382	-16.90	-13.33	8.93	0.27
	2.090(2)	*-16.731(5)*	*1.382*	*-13.95*	*-12.29*	*9.51*	*0.13*
C(6A)-C(7A)	2.148(13)	-19.676(34)	1.404	-16.32	-13.20	9.84	0.24
	2.057(3)	*-16.581(7)*	*1.404*	*-14.26*	*-12.23*	*9.91*	*0.17*
	2.125(30)	-20.322(71)	1.405	-16.72	-13.12	9.52	0.27
	1.993(2)	*-15.42(5)*	*1.406*	*-13.51*	*-11.72*	*9.81*	*0.15*
C(7A)-C(8A)	2.171(13)	-20.131(34)	1.384	-16.48	-13.45	9.80	0.22
	2.106(3)	*-17.671(7)*	*1.384*	*-14.63*	*-12.53*	*9.49*	*0.17*
	2.237(30)	-21.038(74)	1.385	-17.29	-13.45	9.70	0.29
	2.150(2)	*-19.453(6)*	*1.386*	*-15.15*	*-13.26*	*8.96*	*0.14*
C(8A)-C(9A)	2.156(14)	-19.183(36)	1.412	-16.73	-13.85	11.40	0.21
	2.029(3)	*-16.454(7)*	*1.412*	*-14.15*	*-12.52*	*10.21*	*0.13*
	2.059(24)	-17.697(56)	1.411	-15.17	-12.47	9.94	0.22
	2.014(2)	*-16.416(6)*	*1.411*	*-14.40*	*-11.99*	*9.97*	*0.20*
C(9A)-C(10A)	1.893(15)	-13.294(37)	1.469	-14.04	-12.04	12.79	0.17
	1.765(3)	*-11.039(8)*	*1.468*	*-11.98*	*-10.37*	*11.31*	*0.15*
	1.940(24)	-14.921(55)	1.466	-13.91	-12.15	11.14	0.14
	1.795(3)	*-12.133(7)*	*1.465*	*-12.39*	*-10.87*	*11.13*	*0.14*

C(10A)-C(11A)	2.150(13)	-18.078(33)	1.411	-16.30	-13.42	11.64	0.21
	1.992(3)	*-15.051(7)*	*1.410*	*-13.85*	*-11.59*	*10.39*	*0.20*
	2.073(24)	-17.979(53)	1.411	-15.57	-12.62	10.22	0.23
	2.038(2)	*-16.059(6)*	*1.412*	*-14.23*	*-12.20*	*10.37*	*0.17*
C(10A)-C(15A)	2.057(16)	-16.633(44)	1.421	-15.92	-13.24	12.52	0.20
	1.943(3)	*-13.771(8)*	*1.421*	*-13.22*	*-11.52*	*10.97*	*0.15*
	2.074(24)	-17.43(58)	1.423	-14.75	-13.25	10.58	0.11
	1.960(3)	*-14.228(8)*	*1.422*	*-13.78*	*-11.59*	*11.15*	*0.19*
C(11A)-C(12A)	2.195(12)	-19.422(33)	1.385	-16.37	-13.23	10.18	0.24
	2.089(3)	*-17.191(7)*	*1.385*	*-14.58*	*-12.15*	*9.54*	*0.20*
	2.206(29)	-21.029(77)	1.384	-16.65	-13.41	9.03	0.24
	2.063(2)	*-16.608(5)*	*1.384*	*-14.30*	*-11.87*	*9.57*	*0.20*
C(12A)-C(13A)	2.134(13)	-19.278(33)	1.401	-15.73	-13.57	10.02	0.16
	2.026(2)	*-16.227(6)*	*1.401*	*-14.05*	*-11.91*	*9.73*	*0.18*
	2.107(28)	-18.809(67)	1.406	-15.44	-13.20	9.83	0.17
	2.044(2)	*-16.306(5)*	*1.405*	*-13.74*	*-12.29*	*9.72*	*0.12*
C(13A)-C(14A)	2.218(12)	-21.55(32)	1.380	-17.19	-13.88	9.53	0.24
	2.145(3)	*-19.336(7)*	*1.381*	*-15.25*	*-13.14*	*9.06*	*0.16*
	2.157(26)	-20.334(63)	1.384	-16.48	-13.11	9.25	0.26
	2.108(2)	*-17.451(6)*	*1.384*	*-14.58*	*-12.33*	*9.46*	*0.18*
C(14A)-C(15A)	2.094(13)	-17.98(33)	1.408	-16.18	-12.99	11.19	0.24
	2.001(3)	*-15.533(7)*	*1.408*	*-13.99*	*-11.86*	*10.31*	*0.18*
	2.025(24)	-17.085(56)	1.411	-15.13	-11.90	9.95	0.27
	1.991(2)	*-14.783(6)*	*1.411*	*-13.77*	*-11.57*	*10.56*	*0.19*
C(16A)-C(17A)	2.070(21)	-15.664(55)	1.404	-15.67	-13.04	13.05	0.20
	1.984(3)	*-14.853(9)*	*1.404*	*-13.53*	*-11.86*	*10.54*	*0.14*
	2.155(33)	-20.105(92)	1.396	-16.39	-13.24	9.52	0.24
	2.047(3)	*-16.33(8)*	*1.398*	*-13.91*	*-12.54*	*10.12*	*0.11*
	2.138(21)	-17.73(53)	1.400	-16.52	-13.97	12.76	0.18
	2.046(3)	*-16.288(9)*	*1.399*	*-14.25*	*-12.39*	*10.36*	*0.15*

C(16A)-C(21A)	2.040(30)	-17.613(62)	1.403	-15.68	-11.39	9.45	0.38
	2.041(3)	*-16.111(8)*	*1.402*	*-14.19*	*-12.11*	*10.18*	*0.17*
C(17A)-C(18A)	2.198(13)	-19.512(36)	1.391	-16.64	-13.37	10.49	0.24
	2.075(3)	*-16.788(7)*	*1.391*	*-14.32*	*-12.27*	*9.80*	*0.17*
	2.145(16)	-20.671(39)	1.395	-15.24	-12.29	6.86	0.24
	2.053(2)	*-16.35(6)*	*1.395*	*-14.17*	*-12.16*	*9.98*	*0.16*
C(18A)-C(19A)	2.205(21)	-19.299(61)	1.392	-17.21	-14.47	12.38	0.19
	2.088(3)	*-17.672(7)*	*1.392*	*-14.66*	*-12.40*	*9.39*	*0.18*
	2.003(43)	-15.572(68)	1.393	-14.07	-11.75	10.25	0.20
	2.079(2)	*-17.562(6)*	*1.391*	*-14.63*	*-12.32*	*9.39*	*0.19*
C(19A)-C(20A)	2.158(21)	-18.309(52)	1.394	-16.81	-14.01	12.51	0.20
	2.071(3)	*-17.616(8)*	*1.393*	*-14.25*	*-12.46*	*9.09*	*0.14*
	2.078(46)	-17.437(99)	1.395	-16.52	-11.65	10.73	0.42
	2.034(2)	*-16.023(7)*	*1.395*	*-13.95*	*-11.83*	*9.76*	*0.18*
C(19A)-C(22A)	1.854(20)	-13.702(61)	1.500	-13.53	-12.38	12.21	0.09
	1.794(4)	*-12.449(8)*	*1.500*	*-12.42*	*-11.45*	*11.42*	*0.09*
	1.841(48)	-13.178(117)	1.495	-14.64	-13.18	14.65	0.11
	1.804(5)	*-12.64(8)*	*1.497*	*-12.14*	*-11.63*	*11.13*	*0.04*
C(20A)-C(21A)	2.221(13)	-20.143(37)	1.389	-17.03	-13.56	10.45	0.26
	2.062(3)	*-16.813(7)*	*1.389*	*-14.25*	*-12.23*	*9.67*	*0.16*
	2.222(18)	-24.214(43)	1.387	-17.08	-13.07	5.93	0.31
	2.126(3)	*-18.32(7)*	*1.386*	*-14.88*	*-13.11*	*9.67*	*0.14*
F(1B)-C(22B)	2.013(27)	-20.921(146)	1.344	-17.88	-15.79	12.75	0.13
	2.013(5)	*-17.185(22)*	*1.344*	*-16.44*	*-14.48*	*13.74*	*0.14*
	1.840(35)	-13.230(164)	1.344	-13.82	-9.96	10.56	0.39
	1.960(7)	*-16.537(44)*	*1.346*	*-15.71*	*-14.29*	*13.47*	*0.10*
F(2B)-C(22B)	2.038(28)	-19.803(142)	1.346	-17.02	-15.91	13.12	0.07
	1.925(5)	*-14.968(21)*	*1.345*	*-14.73*	*-14.07*	*13.83*	*0.05*
	1.867(36)	-10.769(190)	1.348	-14.04	-12.05	15.32	0.17
	1.842(7)	*-12.396(39)*	*1.362*	*-13.59*	*-12.48*	*13.67*	*0.09*

F(3B)-C(22B)	2.132(29)	-23.752(150)	1.343	-19.11	-18.72	14.08	0.02
	1.868(5)	*-11.248(27)*	*1.340*	*-14.09*	*-12.72*	*15.56*	*0.11*
	2.030(37)	-15.249(207)	1.330	-17.21	-15.25	17.21	0.13
	2.028(8)	*-18.064(46)*	*1.332*	*-16.55*	*-15.01*	*13.49*	*0.10*
N(1B)-C(1B)	2.047(13)	-17.489(56)	1.379	-15.93	-14.31	12.76	0.11
	2.005(4)	*-14.166(17)*	*1.379*	*-14.05*	*-12.30*	*12.18*	*0.14*
	2.160(39)	-21.316(179)	1.379	-17.33	-15.11	11.12	0.15
	2.046(3)	*-14.731(11)*	*1.379*	*-13.92*	*-12.49*	*11.68*	*0.11*
N(1B)-C(2B)	2.192(10)	-21.253(43)	1.368	-16.59	-14.40	9.74	0.15
	2.145(4)	*-18.019(19)*	*1.367*	*-15.80*	*-12.97*	*10.75*	*0.22*
	2.246(35)	-25.167(159)	1.367	-18.97	-14.81	8.61	0.28
	2.127(4)	*-17.766(14)*	*1.365*	*-15.83*	*-13.02*	*11.08*	*0.22*
N(2B)-C(2B)	2.413(15)	-22.931(54)	1.332	-18.88	-16.60	12.55	0.14
	2.395(5)	*-21.173(22)*	*1.332*	*-17.99*	*-16.20*	*13.02*	*0.11*
	2.429(41)	-25.366(170)	1.329	-20.75	-16.56	11.95	0.25
	2.415(4)	*-20.918(16)*	*1.329*	*-18.66*	*-15.80*	*13.54*	*0.18*
N(2B)-C(3B)	2.147(16)	-16.453(62)	1.381	-16.71	-15.07	15.32	0.11
	2.097(3)	*-14.586(12)*	*1.381*	*-14.89*	*-13.28*	*13.59*	*0.12*
	2.144(19)	-17.694(65)	1.382	-15.30	-13.51	11.12	0.13
	2.101(3)	*-14.14(11)*	*1.381*	*-14.71*	*-13.60*	*14.17*	*0.08*
C(1B)-C(3B)	2.221(18)	-20.887(52)	1.383	-17.54	-14.17	10.82	0.24
	2.134(5)	*-18.073(14)*	*1.383*	*-15.45*	*-12.62*	*9.99*	*0.22*
	2.199(35)	-21.219(89)	1.383	-16.47	-13.17	8.43	0.25
	2.139(3)	*-17.666(9)*	*1.383*	*-15.25*	*-12.27*	*9.85*	*0.24*
C(1B)-C(15B)	1.997(15)	-16.677(41)	1.430	-15.41	-13.02	11.75	0.18
	1.907(4)	*-13.99(11)*	*1.429*	*-13.05*	*-11.92*	*10.98*	*0.09*
	1.928(30)	-14.713(70)	1.433	-14.04	-11.77	11.10	0.19
	1.919(3)	*-14.256(8)*	*1.432*	*-13.29*	*-11.47*	*10.51*	*0.16*
	1.900(21)	-14.367(57)	1.466	-14.45	-11.85	11.93	0.22
	1.814(3)	*-13.007(9)*	*1.466*	*-12.68*	*-11.18*	*10.85*	*0.13*

C(2B)-C(16B)	1.832(33)	-14.068(93)	1.466	-14.09	-11.78	11.80	0.20
	1.861(3)	*-13.992(7)*	*1.466*	*-13.09*	*-11.53*	*10.62*	*0.14*
C(3B)-C(4B)	1.991(15)	-17.04(42)	1.435	-15.52	-12.90	11.37	0.20
	1.923(3)	*-15.039(8)*	*1.435*	*-13.74*	*-11.52*	*10.22*	*0.19*
	1.988(19)	-18.243(49)	1.437	-15.14	-11.93	8.83	0.27
	1.908(3)	*-14.348(7)*	*1.437*	*-13.43*	*-11.61*	*10.69*	*0.16*
C(4B)-C(5B)	2.082(13)	-18.189(34)	1.410	-15.95	-13.34	11.10	0.20
	1.991(3)	*-15.718(7)*	*1.410*	*-13.88*	*-11.98*	*10.14*	*0.16*
	2.190(26)	-22.288(62)	1.407	-17.68	-13.66	9.06	0.29
	1.979(2)	*-14.971(6)*	*1.406*	*-13.84*	*-11.41*	*10.28*	*0.21*
C(4B)-C(9B)	2.022(15)	-15.871(41)	1.422	-15.62	-12.61	12.36	0.24
	1.964(3)	*-14.534(8)*	*1.421*	*-13.62*	*-11.75*	*10.85*	*0.16*
	2.014(24)	-17.499(61)	1.425	-14.48	-12.87	9.85	0.13
	1.950(3)	*-14.088(8)*	*1.425*	*-13.39*	*-11.78*	*11.08*	*0.14*
C(5B)-C(6B)	2.252(13)	-21.521(34)	1.381	-17.32	-14.03	9.84	0.23
	2.124(2)	*-18.586(7)*	*1.381*	*-15.11*	*-12.74*	*9.26*	*0.19*
	2.119(28)	-18.765(66)	1.384	-15.72	-12.45	9.40	0.26
	2.112(2)	*-17.628(6)*	*1.386*	*-14.56*	*-12.49*	*9.42*	*0.17*
C(6B)-C(7B)	2.156(12)	-19.756(32)	1.403	-16.23	-13.65	10.12	0.19
	2.033(3)	*-16.373(7)*	*1.404*	*-14.11*	*-12.00*	*9.74*	*0.18*
	2.127(35)	-24.304(126)	1.412	-16.08	-13.32	5.10	0.21
	2.021(2)	*-15.896(6)*	*1.404*	*-13.60*	*-12.03*	*9.74*	*0.13*
C(7B)-C(8B)	2.236(13)	-21.058(34)	1.384	-16.76	-13.95	9.65	0.20
	2.132(3)	*-18.857(7)*	*1.383*	*-14.99*	*-13.03*	*9.16*	*0.15*
	2.160(40)	-15.005(208)	1.381	-18.87	-13.75	17.61	0.37
	2.092(2)	*-16.944(5)*	*1.379*	*-14.32*	*-12.06*	*9.44*	*0.19*
C(8B)-C(9B)	2.088(13)	-18.196(33)	1.411	-16.10	-13.25	11.15	0.22
	2.023(3)	*-16.272(7)*	*1.411*	*-14.26*	*-12.22*	*10.21*	*0.17*
	2.034(25)	-17.412(55)	1.410	-15.47	-11.92	9.98	0.30
	2.024(2)	*-15.634(7)*	*1.409*	*-13.95*	*-12.17*	*10.48*	*0.15*

C(9B)-C(10B)	1.879(15)	-13.26(37)	1.467	-14.15	-11.83	12.71	0.20
	1.771(3)	*-10.743(7)*	*1.466*	*-12.00*	*-10.15*	*11.41*	*0.18*
	1.746(23)	-12.297(69)	1.469	-11.49	-9.59	8.78	0.20
	1.750(3)	*-10.551(7)*	*1.467*	*-11.81*	*-10.19*	*11.45*	*0.16*
C(10B)-C(11B)	2.142(13)	-17.963(32)	1.413	-16.31	-13.29	11.64	0.23
	2.006(2)	*-15.65(7)*	*1.413*	*-14.10*	*-11.91*	*10.36*	*0.18*
	2.079(26)	-20.305(60)	1.409	-16.66	-12.72	9.07	0.31
	2.018(3)	*-16.301(7)*	*1.414*	*-14.21*	*-12.28*	*10.18*	*0.16*
C(10B)-C(15B)	2.057(16)	-16.771(43)	1.420	-15.73	-13.41	12.37	0.17
	1.966(3)	*-14.337(8)*	*1.420*	*-13.42*	*-11.90*	*10.98*	*0.13*
	2.059(24)	-17.927(60)	1.422	-16.14	-12.09	10.31	0.34
	1.938(3)	*-13.662(8)*	*1.419*	*-13.25*	*-11.47*	*11.06*	*0.16*
C(11B)-C(12B)	2.201(12)	-20.455(33)	1.384	-16.50	-13.66	9.70	0.21
	2.119(2)	*-17.699(6)*	*1.384*	*-14.84*	*-12.40*	*9.54*	*0.20*
	2.330(33)	-25.124(92)	1.397	-18.89	-15.85	9.61	0.19
	2.087(2)	*-18.113(6)*	*1.387*	*-14.60*	*-12.52*	*9.00*	*0.17*
C(12B)-C(13B)	2.125(12)	-18.933(32)	1.402	-15.82	-13.24	10.12	0.19
	2.037(2)	*-16.008(6)*	*1.402*	*-13.86*	*-12.12*	*9.97*	*0.14*
	2.058(33)	-20.621(91)	1.412	-16.48	-12.42	8.29	0.33
	2.021(2)	*-16.192(6)*	*1.405*	*-13.69*	*-12.20*	*9.70*	*0.12*
C(13B)-C(14B)	2.234(12)	-21.238(32)	1.379	-16.99	-14.01	9.76	0.21
	2.133(2)	*-18.333(7)*	*1.380*	*-14.88*	*-12.84*	*9.39*	*0.16*
	2.196(30)	-20.818(76)	1.383	-16.47	-13.22	8.87	0.25
	2.108(2)	*-17.238(6)*	*1.382*	*-14.40*	*-12.35*	*9.51*	*0.17*
C(14B)-C(15B)	2.085(13)	-17.9(33)	1.406	-15.71	-13.25	11.07	0.19
	1.995(3)	*-15.417(7)*	*1.406*	*-13.75*	*-11.98*	*10.32*	*0.15*
	2.049(24)	-16.8(58)	1.412	-15.38	-11.64	10.22	0.32
	2.011(2)	*-15.381(6)*	*1.411*	*-13.68*	*-12.07*	*10.37*	*0.13*
	2.114(22)	-16.373(57)	1.404	-16.17	-13.33	13.13	0.21
	2.029(3)	*-15.712(9)*	*1.403*	*-13.96*	*-12.16*	*10.41*	*0.15*

C(16B)-C(17B)	2.111(31)	-19.198(69)	1.400	-16.21	-12.64	9.66	0.28
	2.038(3)	*-15.964(7)*	*1.399*	*-13.88*	*-12.20*	*10.12*	*0.14*
C(16B)-C(21B)	2.139(21)	-17.241(58)	1.400	-16.32	-13.87	12.95	0.18
	2.039(3)	*-16.458(9)*	*1.400*	*-14.47*	*-12.21*	*10.22*	*0.18*
	2.118(33)	-19.539(81)	1.401	-15.87	-13.26	9.59	0.20
	2.030(3)	*-15.892(7)*	*1.401*	*-14.02*	*-12.09*	*10.22*	*0.16*
C(17B)-C(18B)	2.177(13)	-20.697(37)	1.390	-16.72	-13.94	9.97	0.20
	2.033(3)	*-15.952(7)*	*1.390*	*-13.95*	*-11.85*	*9.85*	*0.18*
	2.195(17)	-23.529(41)	1.390	-16.29	-13.08	5.84	0.25
	2.059(2)	*-16.519(6)*	*1.391*	*-14.40*	*-12.05*	*9.94*	*0.19*
C(18B)-C(19B)	2.182(21)	-17.876(59)	1.395	-17.30	-13.49	12.91	0.28
	2.067(3)	*-17.582(7)*	*1.395*	*-14.39*	*-12.35*	*9.16*	*0.17*
	2.158(42)	-19.076(90)	1.390	-16.26	-13.59	10.78	0.20
	2.056(2)	*-17.084(6)*	*1.390*	*-14.60*	*-11.94*	*9.46*	*0.22*
C(19B)-C(20B)	2.187(21)	-17.941(60)	1.391	-17.02	-13.72	12.79	0.24
	2.097(3)	*-17.39(7)*	*1.391*	*-14.64*	*-12.15*	*9.40*	*0.21*
	2.074(40)	-17.48(70)	1.394	-15.54	-12.76	10.82	0.22
	2.058(2)	*-17.167(6)*	*1.394*	*-14.30*	*-12.28*	*9.42*	*0.16*
C(19B)-C(22B)	1.842(19)	-12.298(56)	1.502	-13.63	-12.95	14.28	0.05
	1.792(3)	*-13.513(7)*	*1.502*	*-12.14*	*-11.52*	*10.16*	*0.05*
	1.813(43)	-11.206(96)	1.500	-13.06	-12.04	13.89	0.08
	1.793(5)	*-12.251(8)*	*1.498*	*-12.51*	*-11.14*	*11.40*	*0.12*
C(20B)-C(21B)	2.205(13)	-19.822(37)	1.390	-16.82	-13.49	10.49	0.25
	2.070(3)	*-17.018(7)*	*1.390*	*-14.26*	*-12.45*	*9.69*	*0.14*
	2.172(17)	-22.849(40)	1.391	-15.95	-13.13	6.23	0.21
	2.065(2)	*-16.612(6)*	*1.392*	*-14.36*	*-12.26*	*10.00*	*0.17*

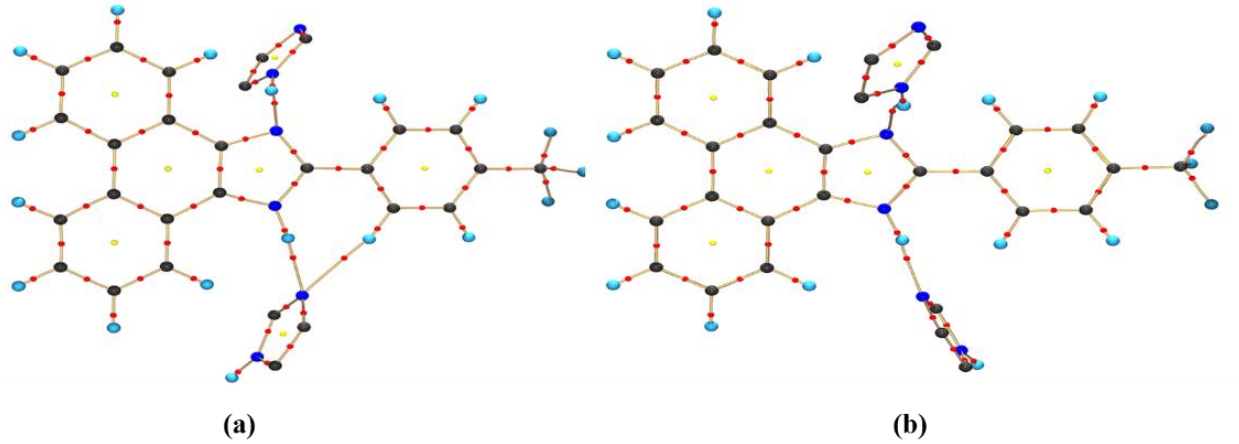

Figure S21: Bond critical points (BCPs) (red spheres), ring critical points (RCPs) (yellow spheres), and bond paths (BPs) (golden line) for the covalent and intermolecular hydrogen bonding in (a) 1P_T and (b) 1P_O polymorphic forms, plotted based on the experimental multipole model.

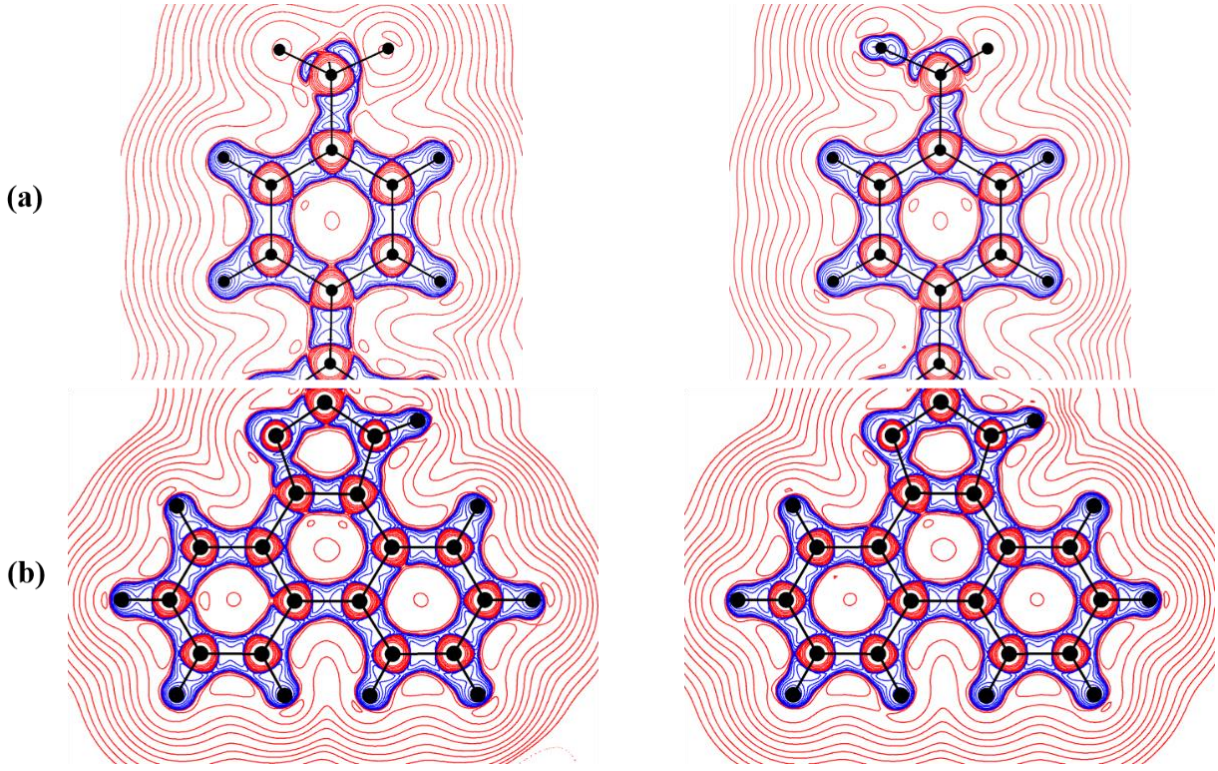

Figure S22: Laplacian maps (experimental) for 1P_T drawn in the plane containing atoms (a) C7, C12, and C2, and (b) C21, C17, and C22 for molecule A (left) and molecule B (right). Contours of Laplacian drawn at a logarithmic interval of $-\nabla^2\rho_b$ e Å^{-5}. Blue and red solid lines represent negative and positive contours, respectively.

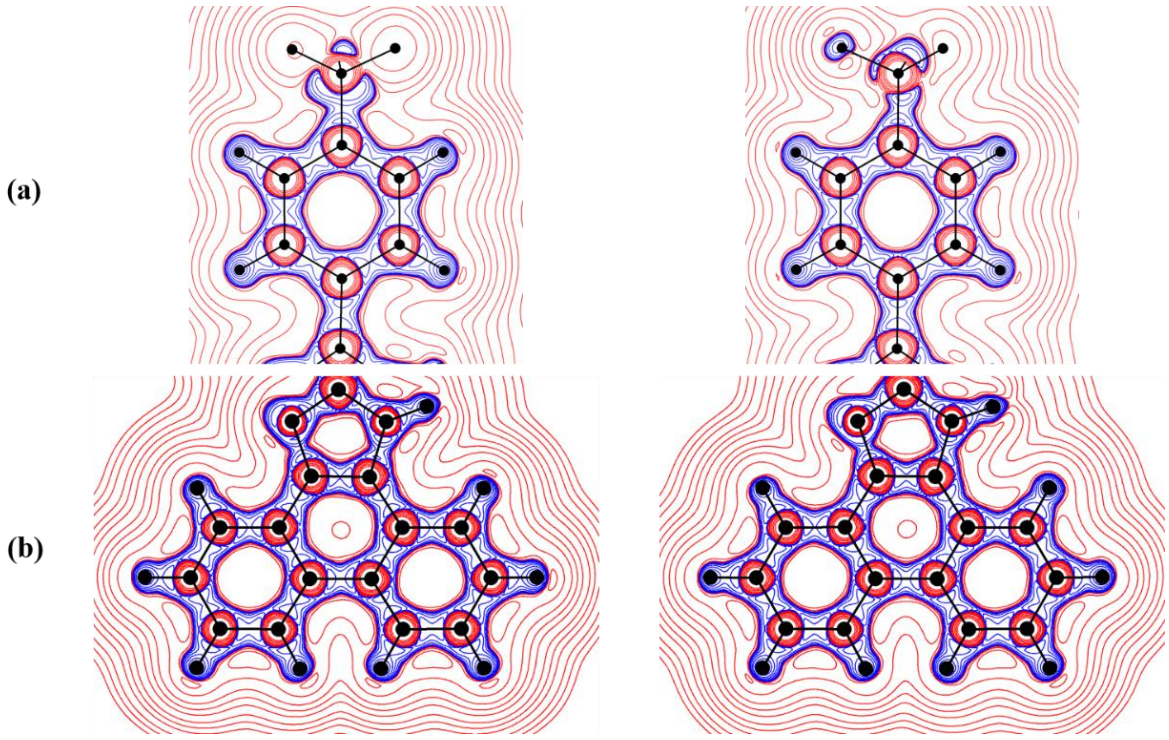

Figure S23: Laplacian maps (theoretical) for 1P_T drawn in the plane containing atoms (a) C7, C12, C2, and (b) C21, C17, C22 for molecule A (left) and molecule B (right).

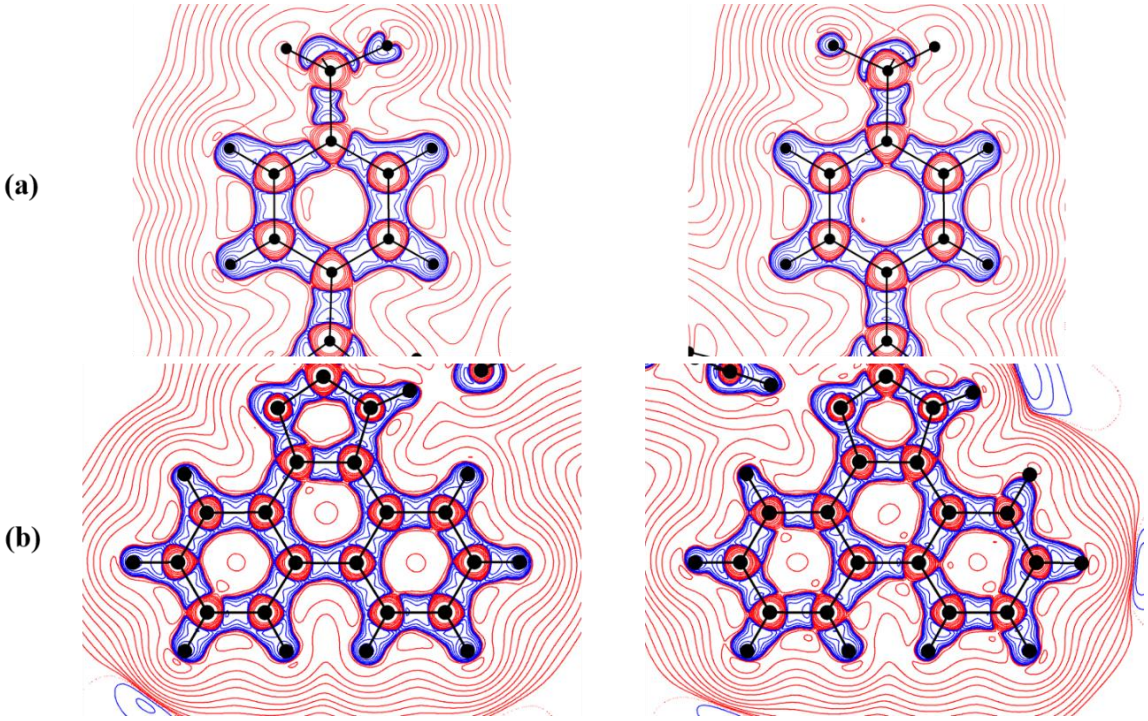

Figure S24: Laplacian maps (experimental) for 1P_O drawn in the plane containing atoms (a) C7, C12, and C2, and (b) C21, C17, and C22 for molecule A (left) and molecule B (right).

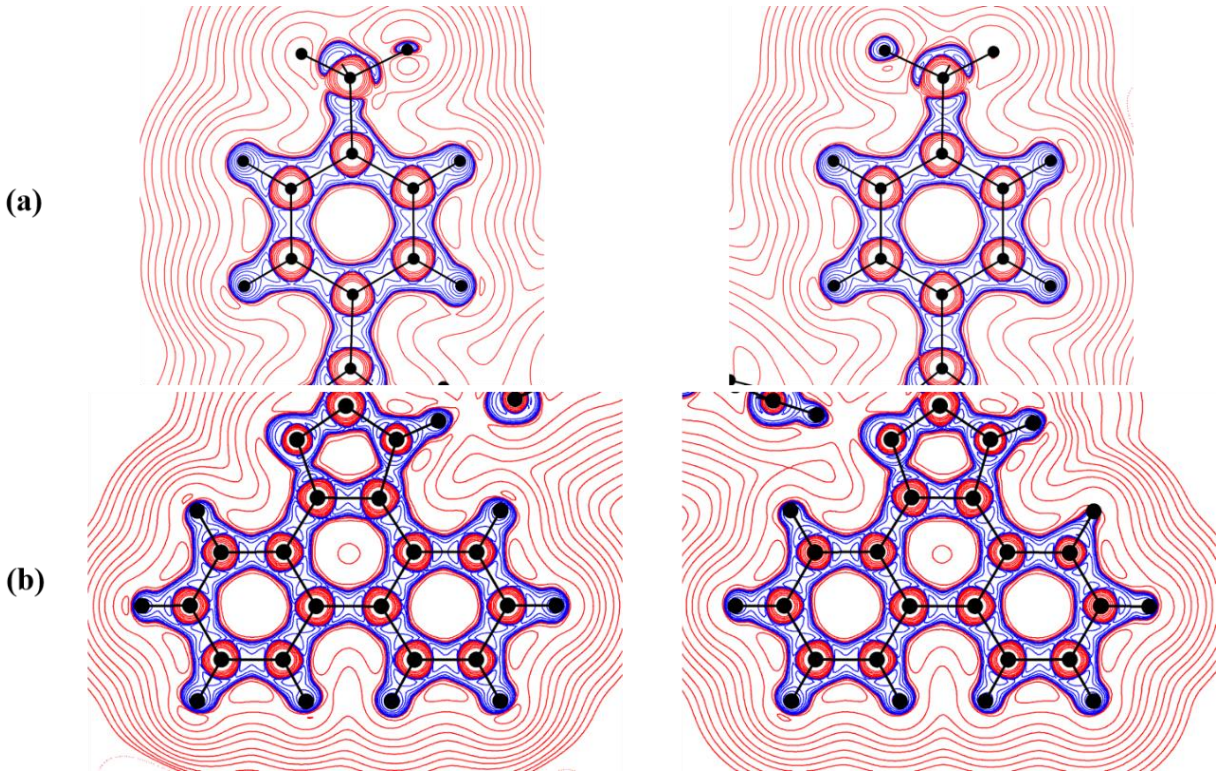

Figure S25: Laplacian maps (theoretical) for 1P_O drawn in the plane containing atoms (a) C7, C12, and C2, and (b) C21, C17, and C22 for molecule A (left) and molecule B (right).

Table S4: Topological parameters of the bonds involved in the proton tautomeric pathways in the polymorphic forms 1P_T (first row) and 1P_O (second row).

Bonds	***ρ* (*e*Å^{-3})**		**$\nabla^2\rho$ (*e*Å^{-5})**		**R_{ij} (Å)**		***ε***		**G_{cp} (r) (kJ mol^{-1} Å^{-3})**		**V_{cp} (r) (kJ mol^{-1} Å^{-3})**	
	Exp.	***Theo.***	***Exp.***	***Theo.***	***Exp.***	***Theo.***	***Exp.***	***Theo.***	***Exp.***	***Theo.***	***Exp.***	***Theo.***
N1A-C1A	2.105	2.052	-19.255	-15.351	1.375	1.374	0.16	0.13	4935.94	5119.73	-13416.31	-13048.74
	1.960	2.034	-17.232	-15.228	1.377	1.379	0.05	0.15	4358.33	5040.96	-11893.52	-12864.95
N1A-C2A	2.201	2.129	-21.181	-18.270	1.366	1.367	0.29	0.21	5277.26	5198.49	-14413.99	-13757.62
	2.195	2.147	-23.753	-19.192	1.363	1.364	0.30	0.14	4909.69	5198.49	-14203.96	-13915.15
N2A-C2A	2.491	2.361	-23.418	-20.975	1.334	1.334	0.16	0.12	6800.05	6274.95	-17905.91	-16383.12
	2.451	2.325	-25.126	-20.758	1.334	1.334	0.19	0.14	6327.46	6064.91	-17275.79	-15963.04
N1A-H1A	2.097	2.136	-32.392	-26.682	1.034	1.034	0.06	0.07	3281.88	4200.80	-12523.64	-13311.29
	2.105	2.070	-33.105	-25.440	1.035	1.034	0.04	0.06	3229.37	3990.76	-12576.15	-12628.66
N1B-C1B	2.047	2.005	-17.489	-14.166	1.379	1.379	0.11	0.14	4830.92	4988.45	-12864.95	-12576.15
	2.160	2.046	-21.316	-14.731	1.379	1.379	0.15	0.11	5014.71	5145.98	-13915.15	-13022.48
N1B-C2B	2.192	2.145	-21.253	-18.019	1.368	1.367	0.15	0.22	5198.49	5329.77	-14308.98	-13967.66
	2.246	2.127	-25.167	-17.766	1.367	1.365	0.28	0.22	5040.96	5251.00	-14729.06	-13757.62
N2B-C2B	2.413	2.395	-22.931	-21.173	1.332	1.332	0.14	0.11	6353.71	6458.73	-16908.22	-16803.20
	2.429	2.415	-25.366	-20.918	1.329	1.329	0.25	0.18	6169.93	6616.26	-16986.99	-17065.75
N1B-H1B	2.166	2.082	-33.751	-27.127	1.040	1.039	0.06	0.08	3518.17	3833.23	-13232.52	-12654.91
	2.172	2.080	-33.610	-28.153	1.039	1.039	0.07	0.07	3570.68	3701.96	-13337.54	-12576.15
H1A…N2B	0.226	0.262	1.843	2.048	1.852	1.854	0.05	0.07	393.83	472.59	-472.59	-577.61
	0.292	0.318	2.303	2.354	1.789	1.785	0.06	0.06	551.36	603.87	-682.63	-761.40
H1B…N2A	0.201	0.237	1.530	1.638	1.902	1.901	0.03	0.01	341.32	393.83	-393.83	-472.59
	0.105	0.212	2.561	1.480	1.978	1.950	0.18	0.04	367.57	341.32	-262.55	-420.08

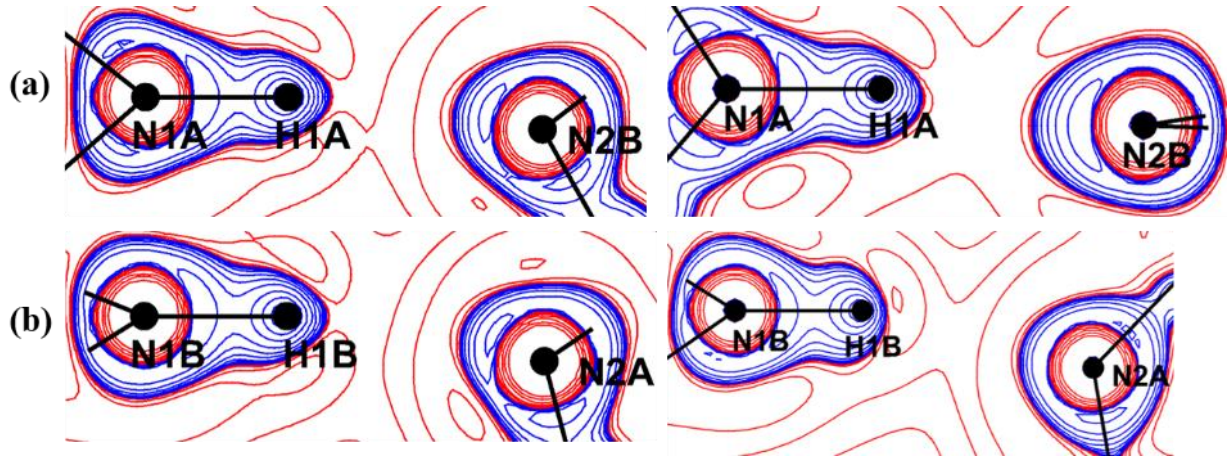

Figure S26: Experimental Laplacian maps of N-H…N hydrogen bonds for 1P_T (left) and 1P_O (right). Contours of Laplacian drawn at a logarithmic interval of $-\nabla^2\rho_b$ eÅ^{-5}. Blue and red solid lines represent negative and positive contours, respectively.

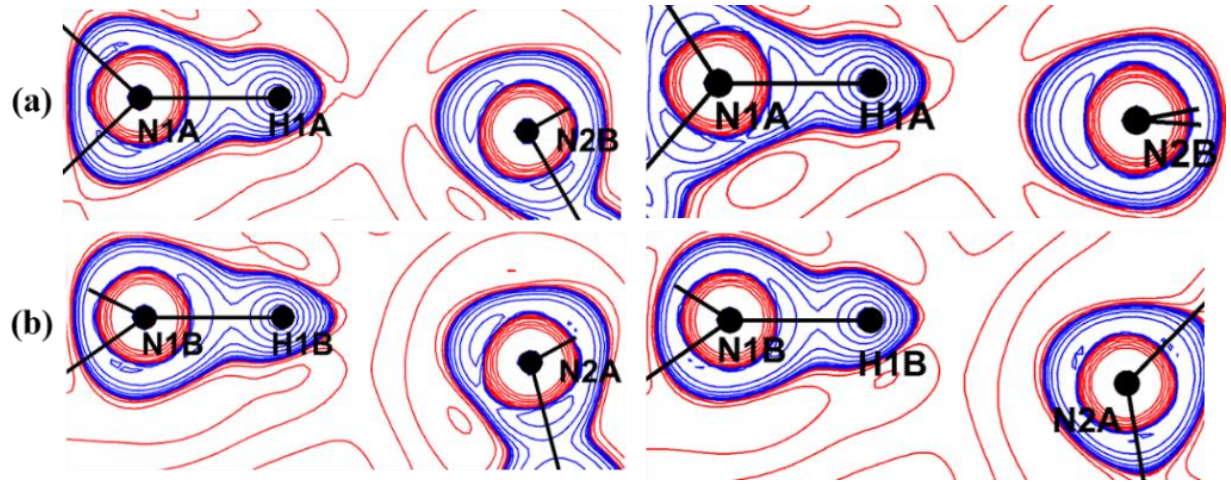

Figure S27: Theoretical Laplacian maps of N-H…N interactions for 1P_T (left) and 1P_O (right). Contours of Laplacian drawn at a logarithmic interval of $-\nabla^2\rho_b$ eÅ^{-5}. Blue and red solid lines represent negative and positive contours, respectively.

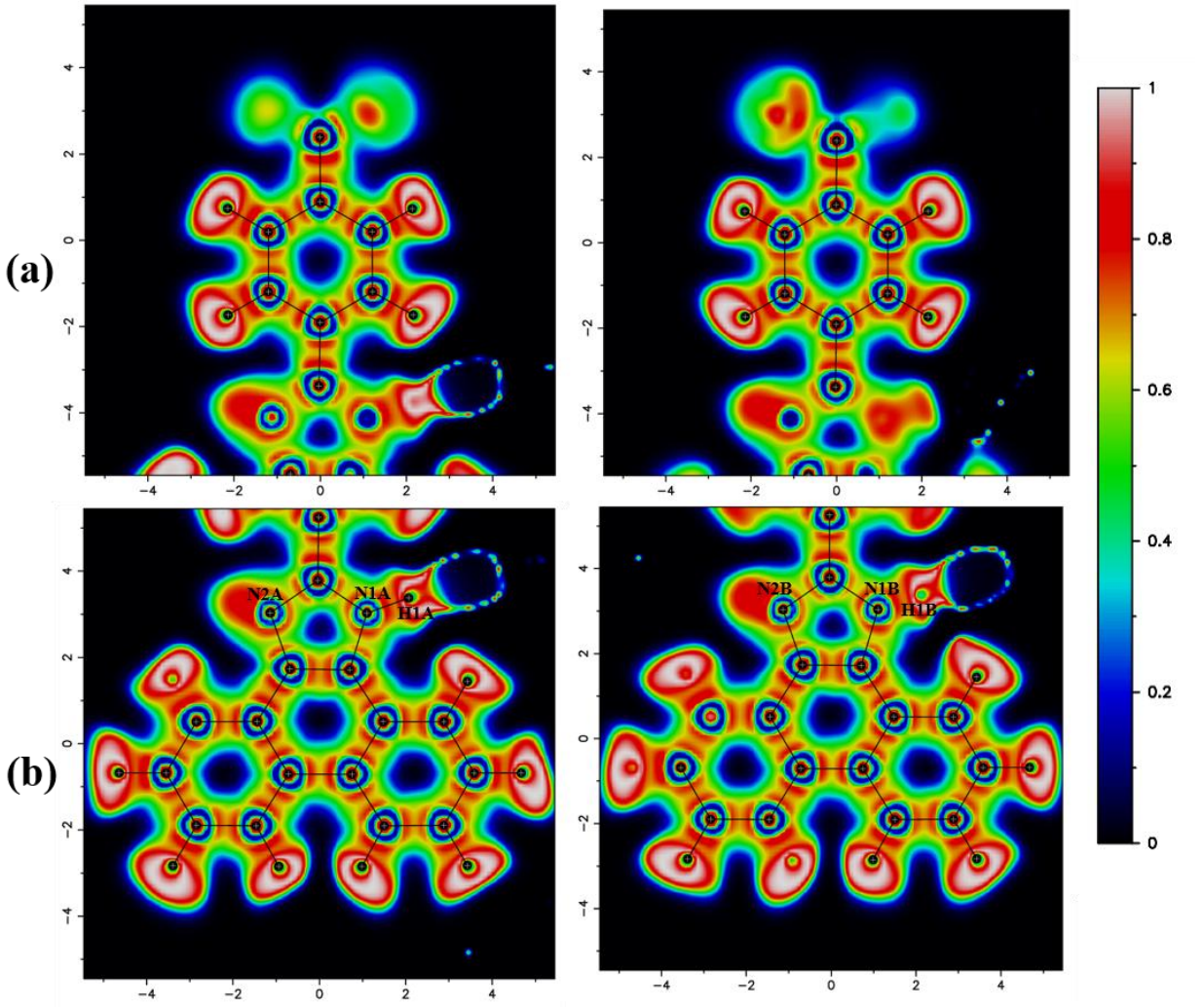

Figure S28: Experimental 2D-ELF for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C7, C12, and C2, and (b) C21, C17, C22 for 1P_T form.

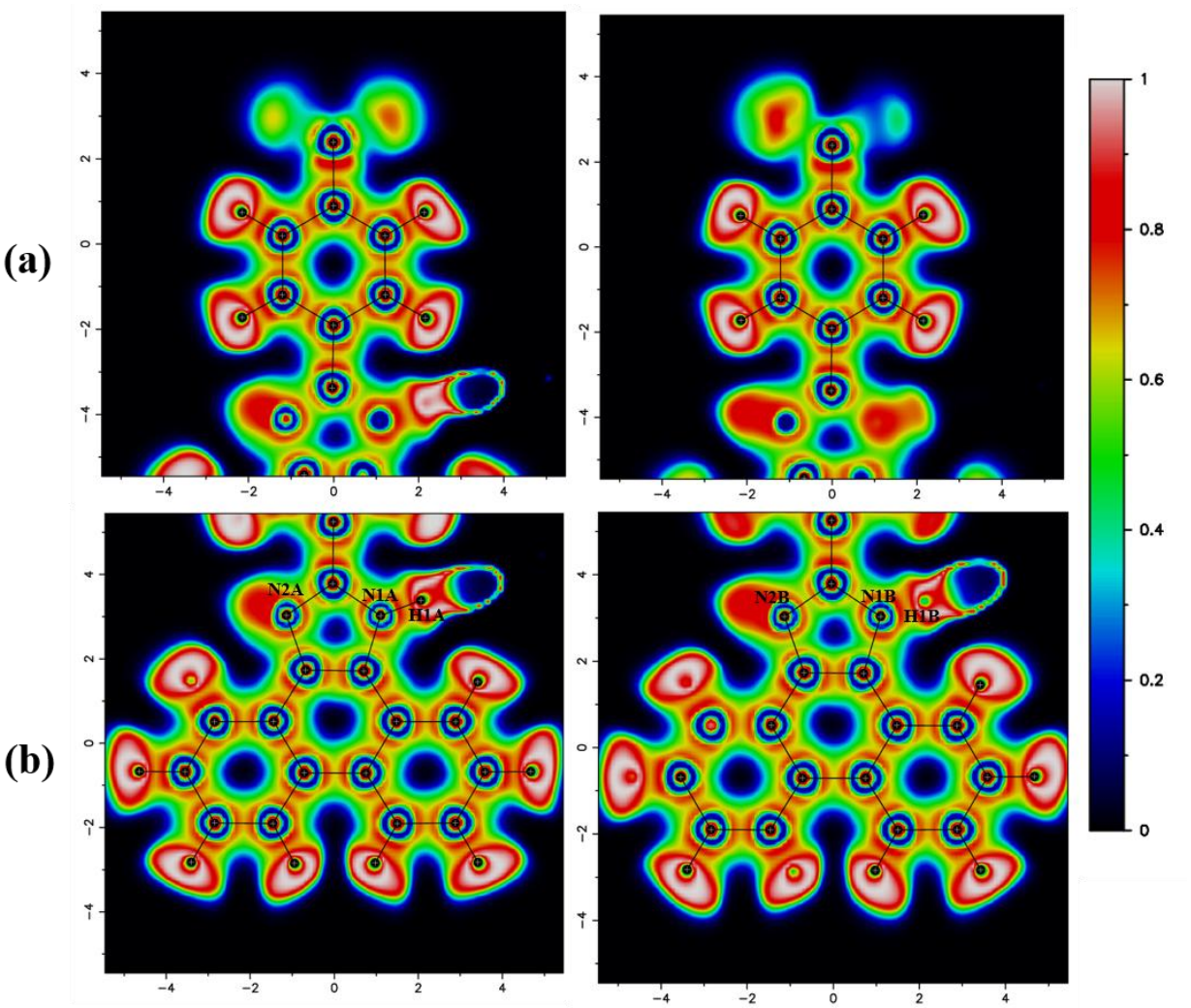

Figure S29: Theoretical 2D-ELF for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C7, C12, C2, and (b) C21, C17, C22 for 1P_T form.

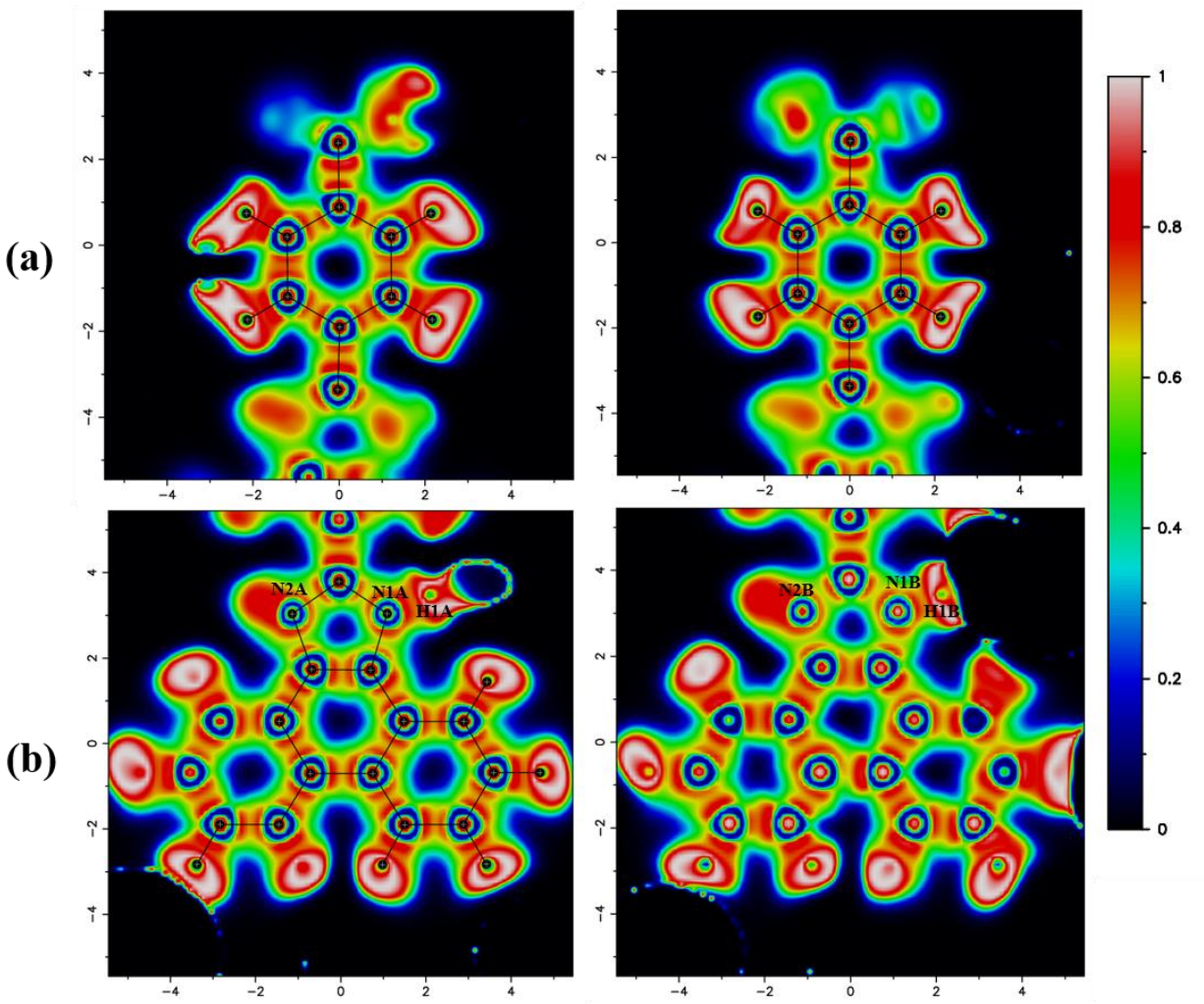

Figure S30: Experimental electron localization function for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C7, C12, C2, and (b) C21, C17, C22 for 1P_O form.

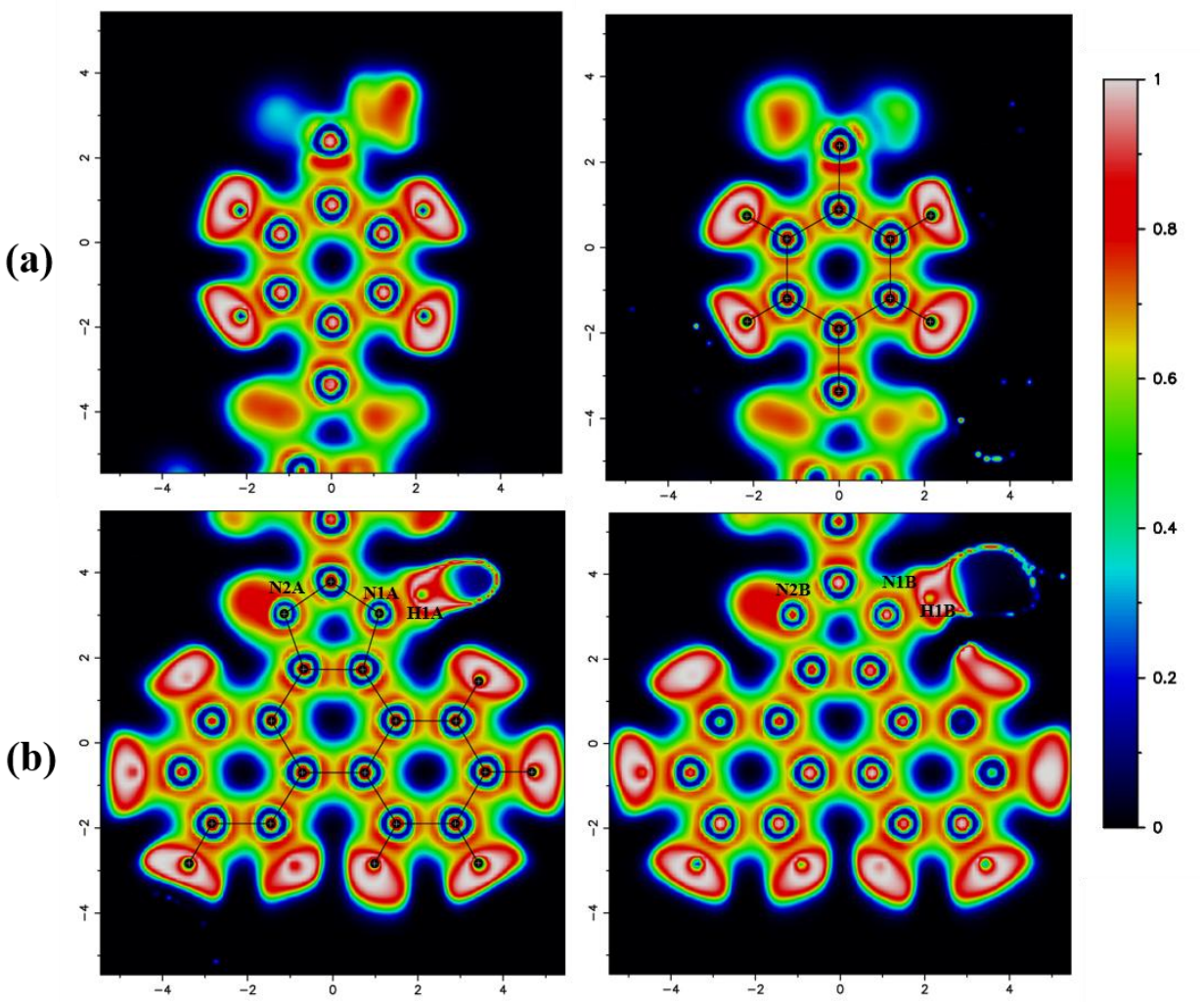

Figure S31: Theoretical electron localization function for molecule A (left) and molecule B (right), drawn in the plane containing atoms (a) C7, C12, C2, and (b) C21, C17, C22 for 1P_O form.

Table S5: Experimental and optimized lattice parameters, N-H and N-H…N distances, and N-H…N angles for the polymorphic forms.

	1P_T				**1P_O**			
Parameters	Pristine Structure (Before Proton Transfer)		Modified Structure (After Proton Transfer)	Difference | Optimized (Pristine – Modified) Structure |	Pristine Structure (Before Proton Transfer)		Modified Structure (After Proton Transfer)	Difference | Optimized (Pristine – Modified) Structure |
	Crystal	Optimized	Optimized		Crystal	Optimized	Optimized	
a (Å)	14.4058	14.4086		0	18.6560	18.4766		0
b (Å)	14.4058	14.4085		0	10.2687	10.2896		0
c (Å)	15.8555	15.7561		0	17.9704	17.9380		0
N1A-H1A (Å)	1.034	1.048	-		1.034	1.060	-	
N2A-H1B (Å)	-	-	1.056	0.008	-	-	1.053	0.007
N1A-H1A…N2B (Å)	1.852	1.803	-		1.785	1.717	-	
N1A…H1A-N2B (Å)	-	-	1.734	0.069	-	-	1.675	0.042
∠N1A-H1A…N2B (˚)	172.73	173.84	-		172.07	176.52	-	
∠N1A…H1A-N2B (˚)	-	-	164.98	8.86	-	-	177.74	1.22
N1B-H1B (Å)	1.039	1.045	-		1.039	1.043	-	
N2B-H1A (Å)	-	-	1.060	0.015	-	-	1.067	0.024
N1B-H1B…N2A (Å)	1.899	1.847	-		1.946	1.879	-	
N1B…H1B-N2A (Å)	-	-	1.797	0.050	-	-	1.826	0.053
∠N1B-H1B…N2A (˚)	170.06	170.01	-		166.07	169.31	-	
∠N1B…H1B-N2A (˚)	-	-	158.26	11.75	-	-	156.23	13.08

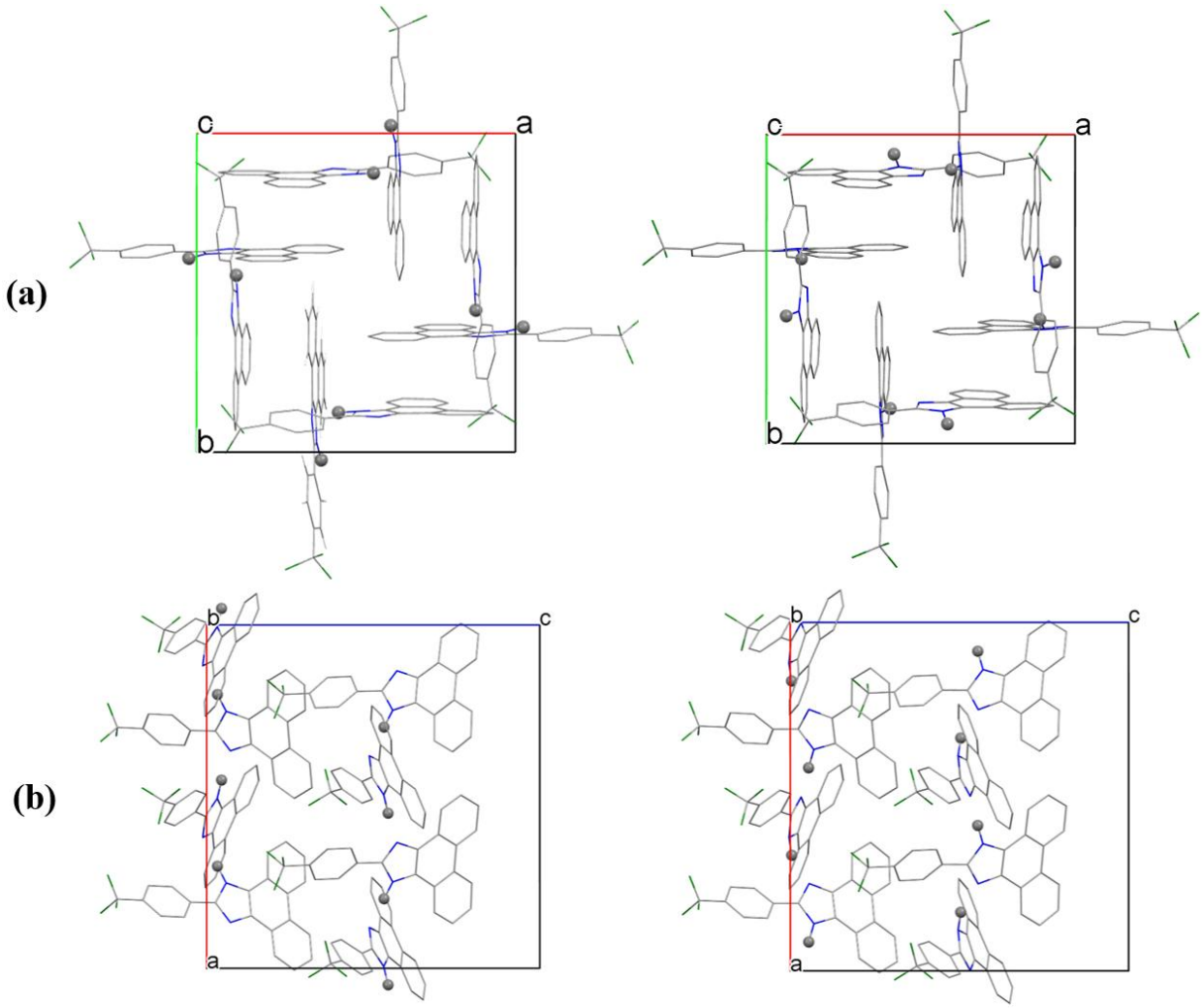

Figure S32: Pristine optimized structure (left) and modified structure (right) for (a) 1P_T and (b) 1P_O form. Only H-atoms (highlighted in grey) of the -NH groups are shown for clarity.

Annexure 1

Optimized coordinates of compound **1**

F	-6.644194000000	-0.088688000000	1.303378000000
F	-6.717761000000	1.147126000000	-0.482844000000
F	-6.744351000000	-1.028912000000	-0.654507000000
N	0.357690000000	-1.137514000000	-0.017723000000
N	0.301408000000	1.095559000000	-0.036445000000
C	4.099892000000	-0.693520000000	0.019893000000
C	-3.986283000000	1.189759000000	0.097072000000
C	4.054605000000	0.776067000000	0.001556000000
C	2.802830000000	1.461466000000	-0.020369000000
C	1.671005000000	-0.720482000000	-0.006742000000
C	-0.434237000000	-0.005546000000	-0.031882000000
C	-1.895907000000	-0.035134000000	-0.039385000000
C	1.606101000000	0.668221000000	-0.021852000000
C	2.891377000000	-1.460221000000	0.014108000000
C	-2.598195000000	1.176000000000	0.097278000000
C	4.149875000000	-3.536785000000	0.050978000000
C	5.344978000000	-2.799221000000	0.058282000000
C	5.314042000000	-1.414317000000	0.042704000000
C	-6.201196000000	0.006131000000	0.026476000000
C	2.753513000000	2.868582000000	-0.038551000000
C	-4.015679000000	-1.213728000000	-0.181702000000
C	-4.699764000000	-0.005416000000	-0.039967000000
C	-2.624719000000	-1.227318000000	-0.184706000000
C	2.939247000000	-2.869795000000	0.029025000000
C	5.223926000000	1.570050000000	0.004125000000
C	5.162038000000	2.953416000000	-0.013708000000
C	3.920066000000	3.610665000000	-0.035232000000
H	-4.523474000000	2.126595000000	0.196568000000
H	-2.031091000000	2.093871000000	0.200144000000
H	4.175849000000	-4.622050000000	0.062199000000
H	6.300161000000	-3.315010000000	0.075725000000
H	6.256720000000	-0.880037000000	0.048380000000
H	1.779637000000	3.346500000000	-0.055378000000
H	-4.572686000000	-2.136057000000	-0.302500000000
H	-2.115908000000	-2.177145000000	-0.320430000000
H	2.012241000000	-3.437529000000	0.021445000000
H	6.200104000000	1.099307000000	0.020123000000
H	6.081603000000	3.531052000000	-0.011222000000
H	3.877805000000	4.695652000000	-0.049409000000
H	0.037015000000	-2.090448000000	0.034888000000