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Supporting information for article:

Insight from electron density and energy framework analysis on the structural features of F*x*-TCNQ (*x* = 0, 2, 4) family of molecules

Rahul Shukla, Christian Ruzié, Guillaume Schweicher, Alan R. Kennedy, Yves H. Geerts, Deepak Chopra and Basab Chattopadhyay

Table of Contents

Table S1: Crystallographic Information Table

Compound Code	**TCNQ**	**F_2-TCNQ**	**F_2'-TCNQ**	**F_4-TCNQ**
Formula	$C_{12}N_4H_4$	$C_{12}N_4H_2F_2$	$C_{12}N_4H_2F_2$	$C_{12}N_4F_4$
CCDC No.	1818664	1818662	1818663	1818665
T(K)	100(2)	100(2)	100(2)	100(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073
Formula Weight	204.19	240.18	240.18	276.16
Crystal System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	C2/c	C2/m	P21/c	Pbca
Z/Z′	4, 0.5	2, 0.25	4, 1	4, 0.5
a (Å)	8.8782(13)	10.1713(19)	9.8303(9)	9.1905(18)
b (Å)	6.9117(10)	5.8670(12)	5.4679(5)	8.0558(17)
c (Å)	16.398(2)	8.8512(17)	19.2479(17)	14.564(3)
α (°)	90	90	90	90
β (°)	98.288(6)	106.969(7)	102.417(5)	90
γ (°)	90	90	90	90
Volume ($Å^3$),	995.8(3), 4	505.20(17), 2	1010.39(16), 4	1078.3(4), 4
$\rho_{calc}(g/cm^3)$	1.362	1.579	1.579	1.701
F(000)	416	240	480	544
$\mu(mm^{-1})$	0.088	0.127	0.127	0.157
$\theta_{min,\ max}(°)$	2.510, 30.560	2.406, 30.547	2.687, 30.647	2.797, 30.570
$h_{min,max}$; $k_{min,max}$; $l_{min,max}$	-11,12; -9,9; -23,23	-11,14; -8,8; -12,12	-14,14; -7,7; -27,27	-13,13; -11,11 ; -20,20
No. of reflections	11008	8822	23312	24791
No. of unique reflections	1519	849	3100	1658
Observed reflections	1097	688	2273	1024
R_all, R_obs	0.0823, 0.0462	0.0622, 0.0469	0.0798, 0.0509	0.1403, 0.0708
wR_2_all, wR_2_obs	0.1180, 0.1083	0.1091, 0.1018	0.1240, 0.1110	0.1330, 0.1147
$\Delta\rho_{min,\ max}$ ($e/Å^3$)	-0.26,0.31	-0.28,0.45	-0.37, 0.40	-0.37,0.36
G.o.F	1.059	1.095	1.045	1.119

Theoretical Multipolar Refinement				
$(Sin\theta/\lambda)_{max}(Å^{-1})$	1.407	1.407	1.407	1.407
Reflections used [$I > 0\sigma$]	11620	6173	23600	12585
No of parameters	92	162	310	172
$R(F^2)$,$wR(F^2)$	0.0143, 0.0949	0.0121, 0.0054	0.0124, 0.008	0.0110, 0.0065
$\Delta\rho_{min,\ max}$ $(e/Å^3)$	-0.06,0.08	-0.13,0.15	-0.09,0.12	-0.07,0.09

Table S2: Previous reported structures of TCNQ, F_2-TCNQ and F_4-TCNQ

Molecule	**Refcode**	**Space Group**	**T(K)**	**Unit cell parameters [*a*(Å), *b*(Å), *c*(Å), *β*(°)]**
TCNQ	TCYQME	*C*2/*c*	295	8.906, 7.060, 16.395, 98.53
	TCYQME01	*C*2/*c*	110	8.865(2), 6.883(1), 16.387(1), 98.21(3)
	TCYQME02	*Cc*	295	8.910(4), 7.068(1), 16.403(1), 98.51
	TCYQME03	*C*2/*c*	180	8.883(0), 6.954(0), 16.395(0), 98.35(0)
	TCYQME04	*C*2/*c*	150	8.883(0), 6.927(0), 16.402(1), 98.31(0)
	TCYQME05	*C*2/*c*	150	8.883(0), 6.927(0), 16.402(1), 98.31(0)
	TCYQME06	*C*2/*c*	100	8.884(1), 6.904(0), 16.421(2), 98.24(0)
	TCYQME07	*C*2/*c*	100	8.896(2), 6.913(1), 16.439(5), 98.29(0)
	TCYQME08	*C*2/*c*	150	8.875(0), 6.934(0), 16.407(0), 98.31(0)
F_2-TCNQ	BERZON	*C*2/*m*	295	10.208(4), 6.026(2), 8.836(3), 106.64(3)
	BERZON01	*C*2/*m*	-	10.208(4), 6.026(2), 8.836(3), 106.64(3)
	BERZON0202	*C*2/*m*	180	10.197(0), 5.923(0), 8.836(0), 106.83(0)
	BERZON03	*C*2/*m*	100	10.175(0), 5.855(0), 8.840(0), 106.94(0)
F_4-TCNQ	BAKPAE	*Pbca*	295	14.678(7), b:9.337(5), c:8.174(2), 90
	BAKPAE01	*Pbca*	180	9.246(0), 8.096(0), 14.612(0), 90
	BAKPAE02	*Pcab*	150	8.083(0), 9.223(0), 14.597(0), 90

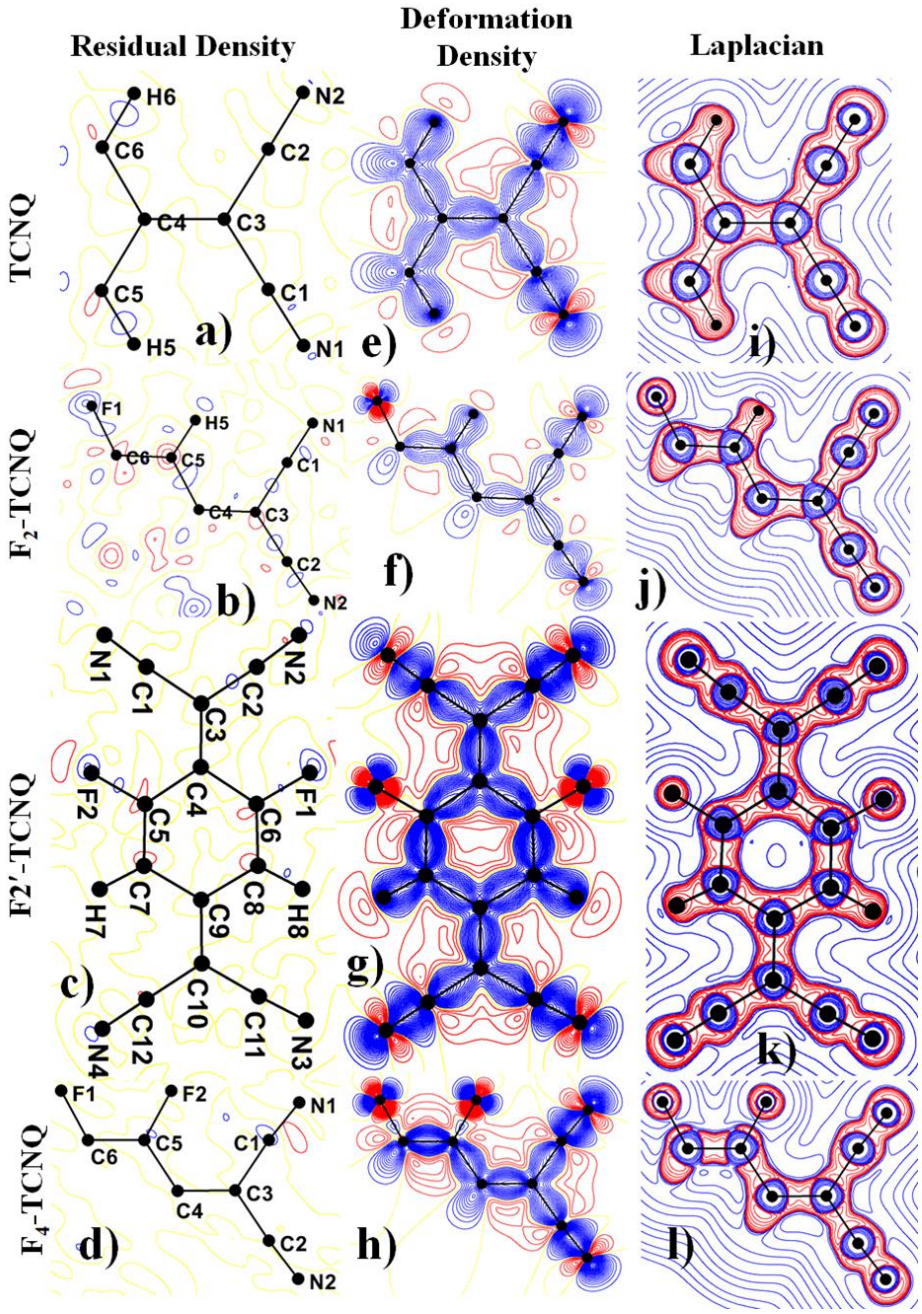

Figure S1(a)-(d) Theoretical residual density, (e)-(h) 2D deformation maps and (i)-(l) 2D Laplacian maps. Contours are drawn at the intervals of ±0.05 e Å^{-3}in case of residual and deformation maps. Laplacian is drawn in logarithmic contours.

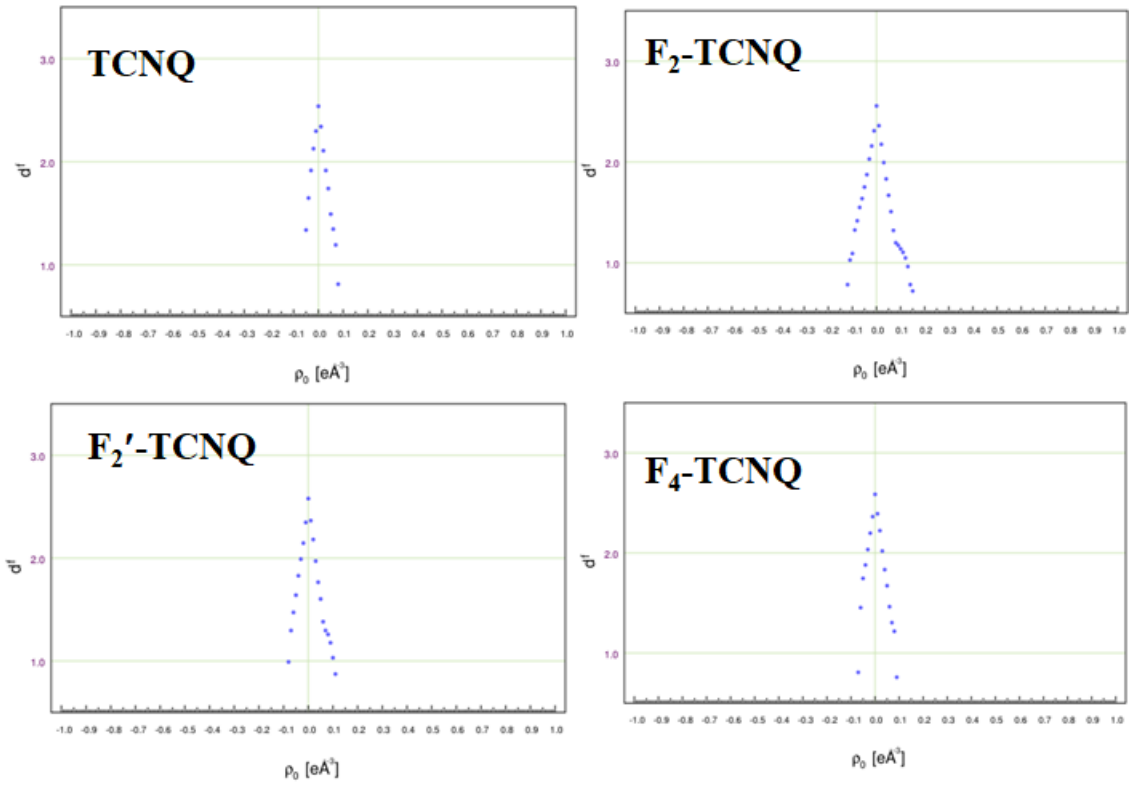

Figure S2 Plot of fractal dimension (d^f) vs residual density (ρ_0)

Table S3 Topological parameters for intramolecular bonds of TCNQ (asymmetric unit)

Bond	R_{ij} (Å)	ρ (e/Å^3)	$\nabla^2\rho$ (e/Å^5)	λ_1	λ_2	λ_3	ε
C1-N1	1.1471	3.2463	-19.24	-24.07	-24.02	28.85	0.00
C2-N2	1.1487	3.2381	-19.69	-24.01	-23.80	28.12	0.01
C1-C3	1.4360	1.8319	-12.16	-12.96	-11.45	12.24	0.13
C2-C3	1.4365	1.8183	-12.23	-12.80	-11.52	12.09	0.11
C3-C4	1.3772	2.1314	-17.87	-15.90	-13.03	11.05	0.22
C4-C5	1.4460	1.8887	-13.46	-13.15	-12.03	11.72	0.09
C4-C6	1.4496	1.8716	-13.03	-13.03	-11.82	11.81	0.10
C5-C6	1.3465	2.2364	-19.09	-16.94	-13.23	11.08	0.28
C5-H5	1.0674	1.8292	-16.14	-17.05	-16.72	17.63	0.02
C6-H6	1.0674	1.8288	-16.15	-17.06	-16.72	17.63	0.02

Table S4 Topological parameters for intramolecular bonds of F_2-TCNQ (asymmetric unit)

Bond	R_{ij} (Å)	ρ (e/Å^3)	$\nabla^2\rho$ (e/Å^5)	λ_1	λ_2	λ_3	ε
C1-N1	1.1466	3.2799	-20.03	-24.69	-24.54	-29.20	0.01
C2-N2	1.1459	3.2544	-15.34	-24.70	-24.41	33.78	0.01

C1-C3	1.4377	1.7912	-10.81	-12.53	-11.03	12.74	0.13
C2-C3	1.4329	1.8199	-11.40	-12.73	-11.54	12.87	0.10
C3-C4	1.3750	2.1349	-18.11	-16.19	-12.77	10.85	0.27
C4-C5	1.4405	1.8399	-12.18	-13.15	-11.49	12.46	0.14
C4-C6	1.4453	1.9017	-14.48	-13.38	-11.69	10.59	0.14
C5-C6	1.3405	2.2904	-19.46	-18.15	-13.81	12.50	0.31
C5-H5	1.0696	1.8787	-16.40	-18.23	-17.57	19.40	0.03
C6-F1	1.3432	1.7666	-7.06	-11.75	-11.74	16.43	0.00

Table S5 Topological parameters for intramolecular bonds of F_2'-TCNQ (asymmetric unit)

Bond	**R_{ij} (Å)**	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**λ_1**	**λ_2**	**λ_3**	**ε**
C1-N1	1.1477	3.2822	-25.38	-24.75	-24.4	23.77	0.01
C2-N2	1.1433	3.3105	-21.61	-25.68	-25.26	29.33	0.02
C11-N3	1.1493	3.2836	-24.13	-24.67	-24.32	24.86	0.01
C12-N4	1.1464	3.2727	-22.90	-24.63	-23.75	25.48	0.04
C1-C3	1.4379	1.8090	-11.71	-12.79	-11.43	12.51	0.12
C2-C3	1.4386	1.7888	-11.13	-12.49	-11.34	12.70	0.10
C3-C4	1.3750	2.1211	-17.39	-16.26	-12.69	11.56	0.28
C4-C5	1.4482	1.8987	-13.86	-13.96	-11.88	11.97	0.17
C4-C6	1.4461	1.8987	-14.37	-13.98	-12.10	11.71	0.15
C5-C7	1.3397	2.3364	-21.55	-18.83	-14.14	11.42	0.33
C5-F2	1.3407	1.7932	-8.35	-12.27	-11.92	15.83	0.03
C6-F1	1.3371	1.8002	-9.07	-12.41	-12.29	15.63	0.01
C7-H7	1.0688	1.8360	-16.32	-17.83	-17.22	18.73	0.04
C6-C8	1.3385	2.3316	-21.75	-18.70	-14.12	11.07	0.32
C8-H8	1.0787	1.9426	-17.27	-19.49	-18.79	21.02	0.04
C7-C9	1.4399	1.8732	-13.31	-13.80	-11.97	12.45	0.15
C8-C9	14353	1.9063	-13.56	-13.91	-12.22	12.57	0.14
C9-C10	1.3758	2.1165	-17.39	-16.22	-12.62	11.46	0.29
C10-C11	1.4307	1.8455	-12.27	-13.01	-11.81	12.55	0.10
C10-C12	1.4304	1.8446	-12.76	-13.14	-11.97	12.35	0.10

Table S6 Topological parameters for intramolecular bonds of F_4-TCNQ (asymmetric unit)

Bond	**R_{ij} (Å)**	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**λ_1**	**λ_2**	**λ_3**	**ε**
C1-N1	1.1445	3.3149	-22.23	-25.58	-25.30	28.65	0.01
C2-N2	1.1422	3.2990	-21.23	-24.98	-24.97	28.63	0.00
C1-C3	1.4377	1.8021	-11.06	-12.46	-11.40	-12.79	0.09
C2-C3	1.4370	1.8045	-11.28	-12.40	-11.44	12.56	0.08
C3-C4	1.3679	2.1331	-17.81	-16.34	-12.76	11.29	0.28
C4-C5	1.4396	1.9128	-13.97	-14.27	-11.87	12.18	0.20
C4-C6	1.4339	1.9346	-14.50	-14.48	-12.12	12.11	0.19
C5-C6	1.3382	2.3613	-22.53	-20.03	-14.04	11.53	0.43
C5-F2	1.3339	1.8750	-11.01	-14.07	-13.50	16.55	0.04
C6-F1	1.3360	1.8805	-11.46	-14.16	-13.78	16.48	0.28

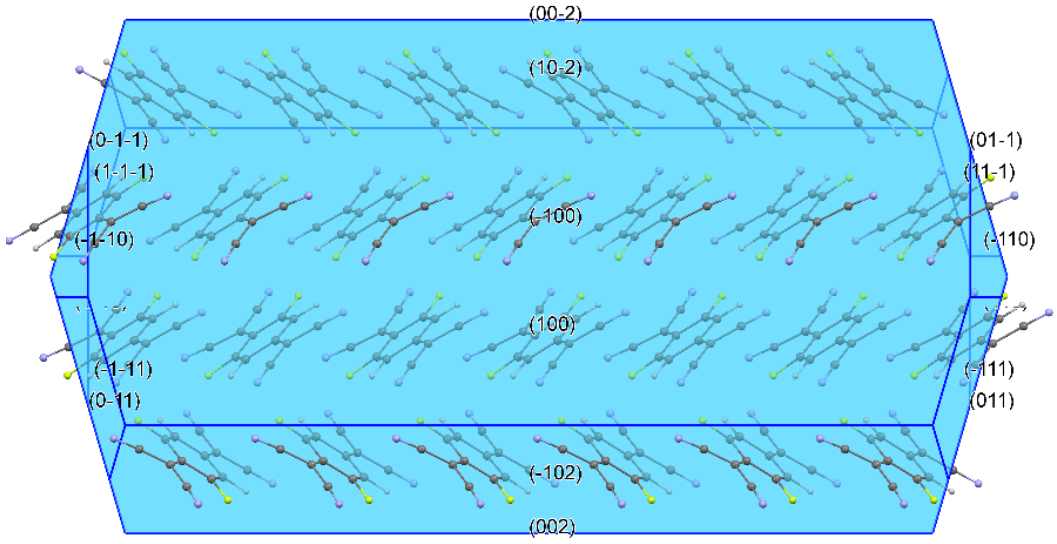

Figure S3BFDH morphology obtained for F2′-TCNQ

Table S7: Geometrical parameters, interaction energies and topological parameters for intermolecular interactions along the transport plane of TCNQ, F_2-TCNQ, F_2′-TCNQ and F_4-TCNQ

Motif	Interaction	Symmetry	Dist. (Å)	∠(°)	R_{ij}(Å)	ρ (e/Å^3)	$\nabla^2\rho$ (e/Å^5)	E_{elec} (kJ/mol)	E_{disp} (kJ/mol)	E_{rep} (kJ/mol)	E_{total} (kJ/mol)

TCNQ											
I	C6-H6···N2	1-x,2-y,1-z	2.38	159	2.7189	0.0566	1.10	-32.0	-9.5	14.4	-27.1
	N2···N2		3.371(2)		3.3814	0.0249	0.36				
II	C6···C6	1.5-x,1.5-y,1-z	3.409(2)		3.7926	0.0347	0.39	-5.3	-30.1	12.2	-23.2
III	C6···C6	1.5-x,2.5-y,1-z	3.561(1)		3.9475	0.0263	0.33	-3.7	-24.7	11.0	-17.4
	C5-H5···N2	-0.5+x,0.5+y,z	3.09	98	3.5011	0.0319	0.40				
	N2···C1		3.384(1)		3.6621	0.0262	0.36				
F_2-TCNQ											
I	N2…C5	0.5+x,0.5+y,z	3.236(1)		3.4298	0.0309	0.39	-13.2	-28.7	13.1	-28.8
	F1…F1	1.5-x,0.5+y,2-z	2.973(1)		2.9794	0.0270	0.50				
II	C5-H5…N1	1-x,y,1-z	2.33	161	2.6624	0.0512	0.72	-32.9	-10.5	17.2	-26.2
	N1…N1		3.268(2)		3.2772	0.0226	0.32				
III	N1…N1	0.5-x,-0.5+y,1-z	3.617(2)		4.6172	0.0310	0.39	-13.7	-14.1	9.9	-17.9
F_2'-TCNQ											
I	N3···C12	x, 1+y, z	3.346(2)	-	3.4660	0.0273	0.37	-6.6	-28.4	10.8	-24.2
	N3···C7		3.476(2)	-	3.7537	0.0280	0.35				
	F2···C8		3.321(2)	-	3.4078	0.0276	0.40				
	F1···N1		3.937(2)	-	3.6209	0.0353	0.54				
	N1···C2		3.236(2)	-	3.3591	0.0336	0.47				
II	N4···C12	1-x,0.5+y,0.5-z	3.078(2)	-	3.4377	0.0492	0.68	-21.1	-12.7	11.5	-22.3
	C7-H7···N4		2.49	166	2.4974	0.0347	0.82				
III	C8-H8···N3	1-x,1-y,-z	2.82	105	3.7628	0.0414	0.57	-14.7	-13.4	7.8	-20.3
F_4-TCNQ											
I	C2…C2	1-x,1-y,1-z	3.328(3)		3.9706	0.0402	0.50	-24.2	-20.2	10.4	-34.0
II	F1…F2	0.5-x,0.5+y,z	2.948(2)		3.0058	0.0351	0.66	-12.2	-24.8	14.5	-22.5
	F2…N1		3.060(2)		3.1503	0.0370	0.62				