Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Entropy-Ruled Nonequilibrium Charge Transport in Thiazolothiazole-Based Molecular Crystals: A Quantum Chemical Study

M. Pavalamuthu and K. Navamani*

Department of Physics, Centre for Research and Development (CFRD)
KPR Institute of Engineering and Technology
Coimbatore – 641407, India

*Corresponding author: pranavam5q@gmail.com

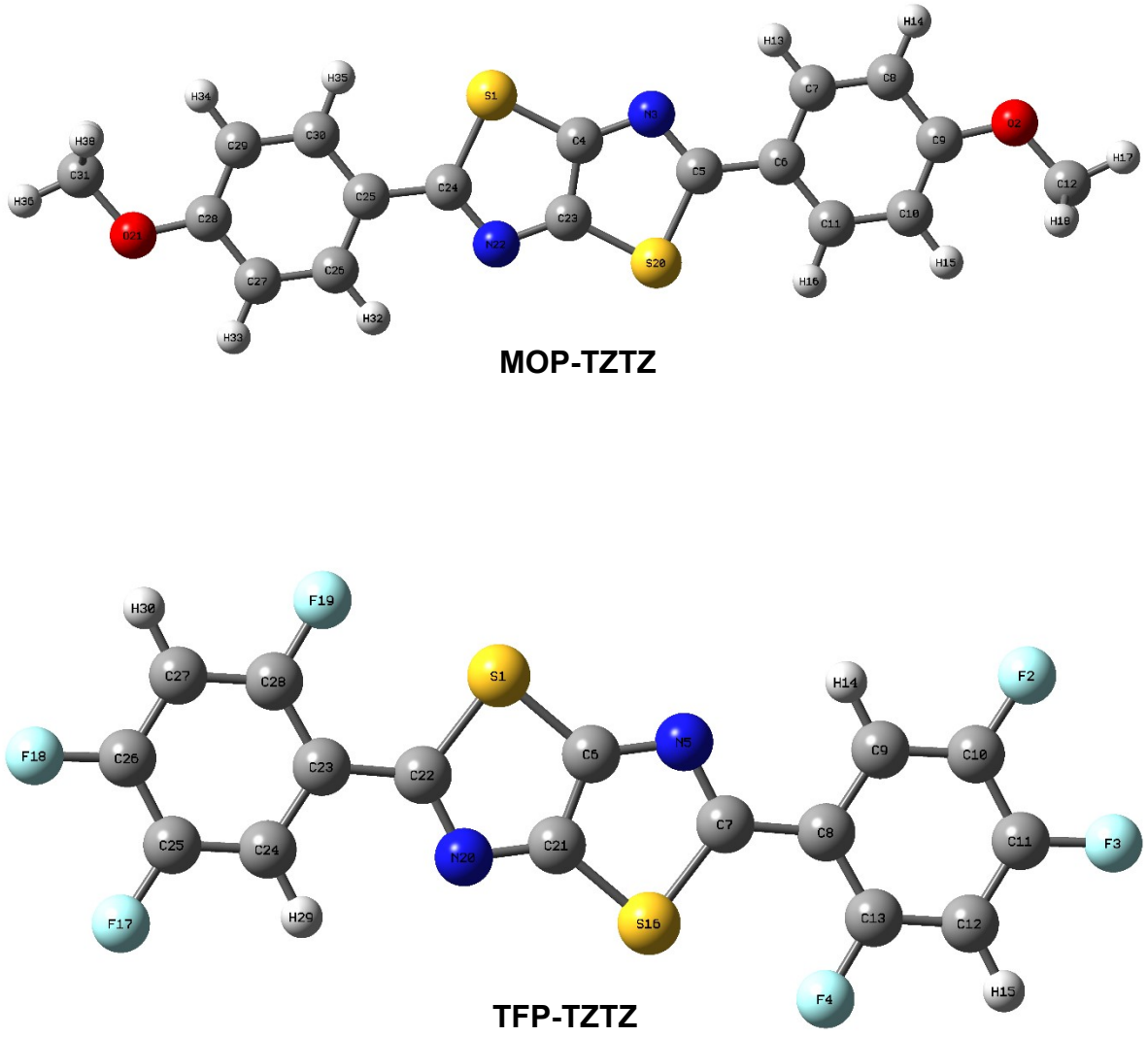

Fig. S1 Optimized molecular structures of MOP-TZTZ and TFP-TZTZ.

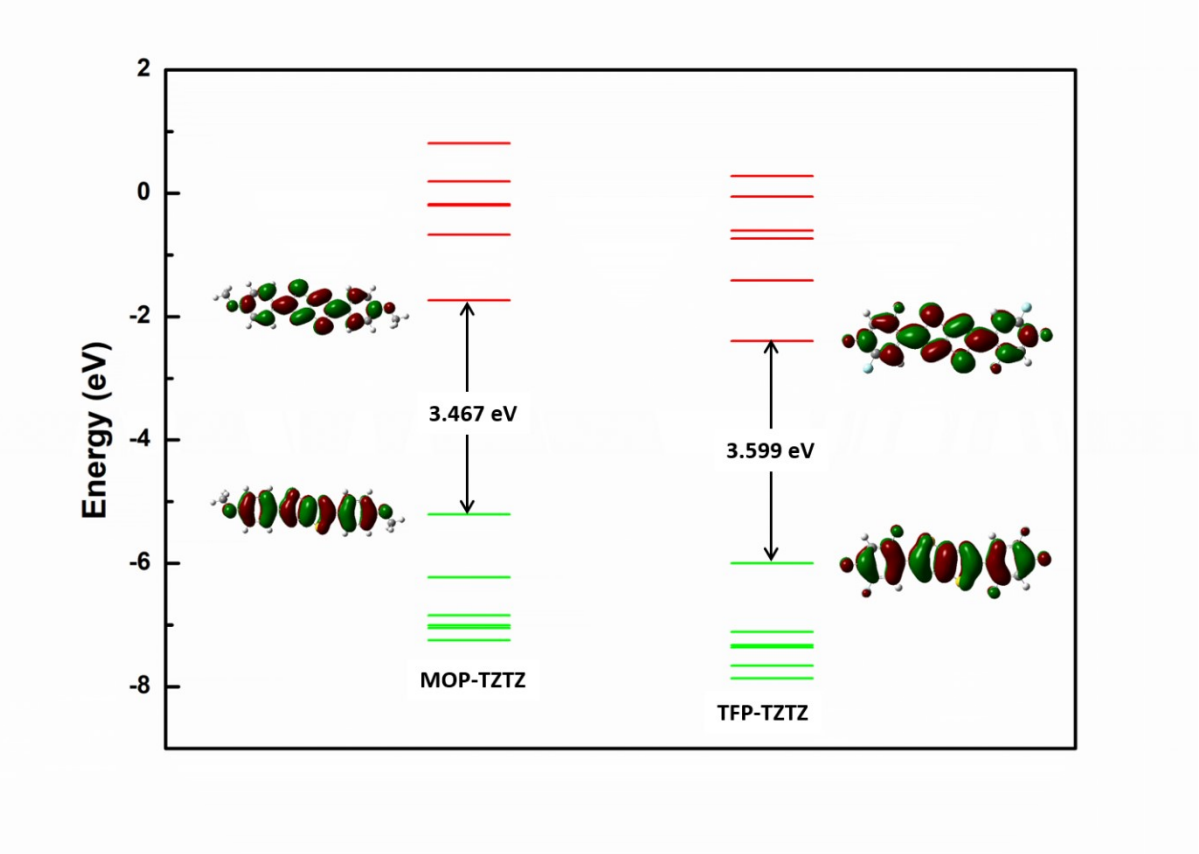

Fig. S2 Energy levels (HOMO and LUMO) diagram of MOP-TZTZ and TFP-TZTZ molecules and their corresponding energy gap.

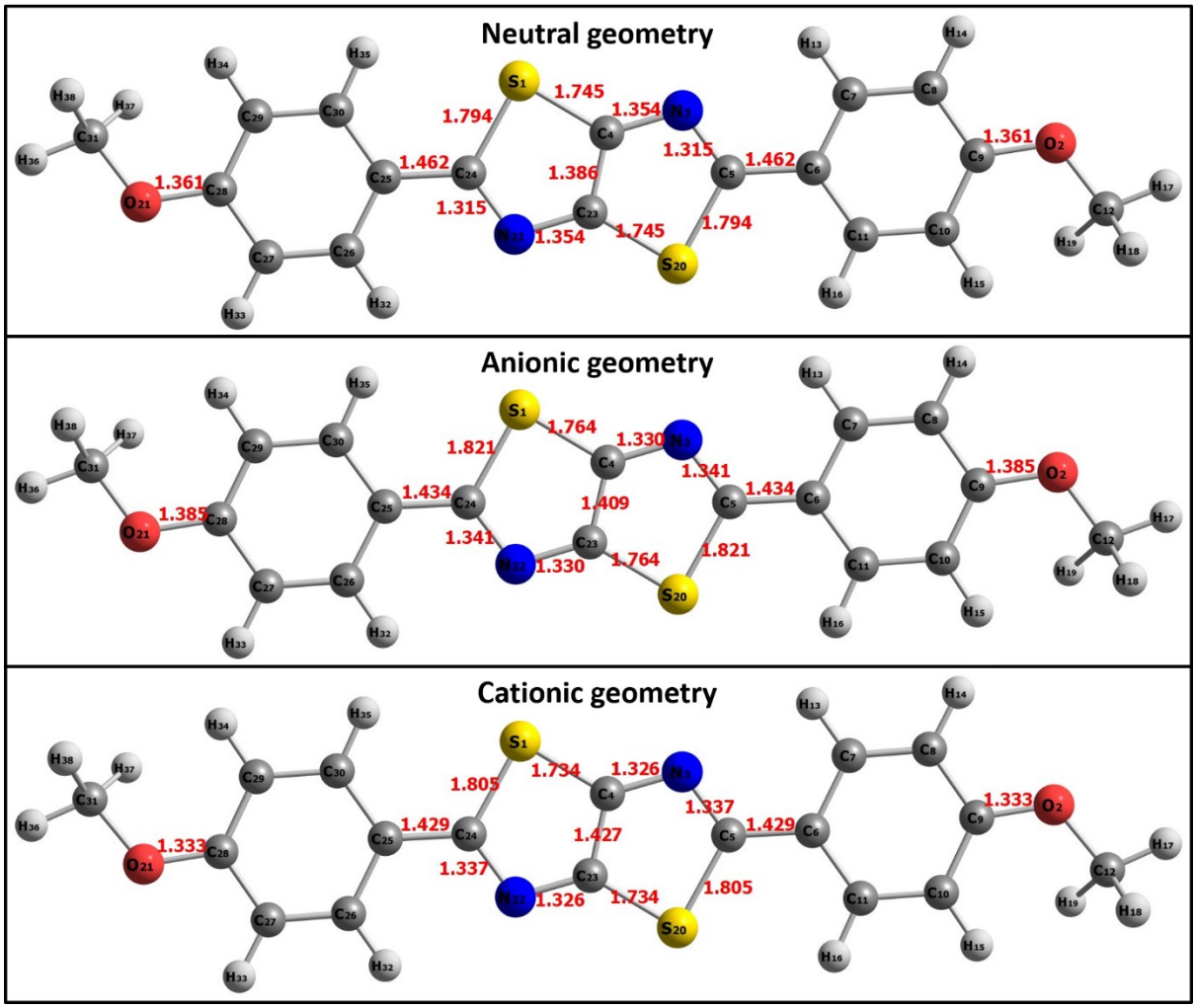

Fig. S3 Calculated bond lengths, in Å, of MOP-TZTZ in optimized neutral, anionic, and cationic geometries for selected atomic specifications.

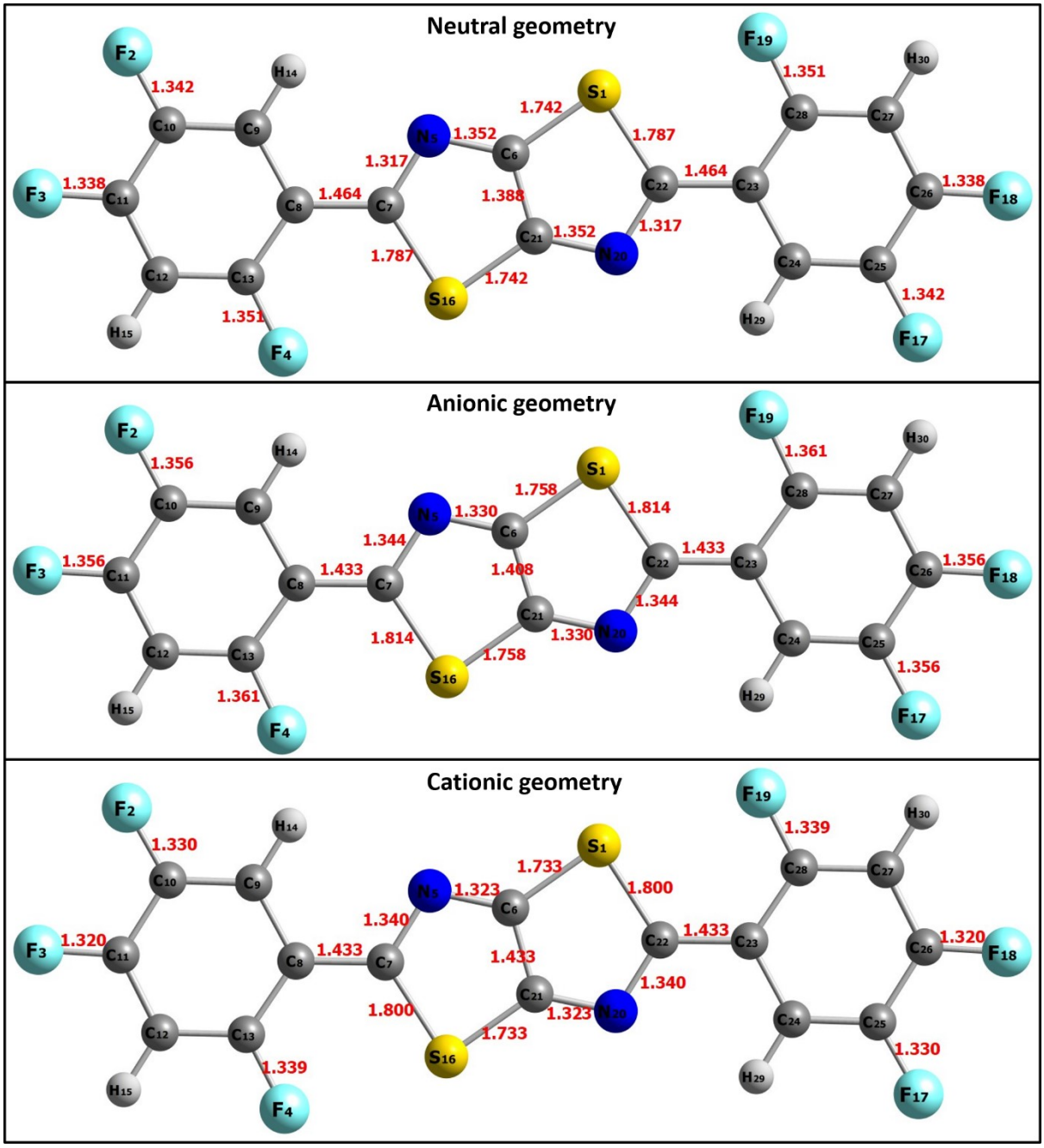

Fig. S4 Calculated bond lengths, in Å, of TFP-TZTZ in optimized neutral, anionic, and cationic geometries for selected atomic specifications.

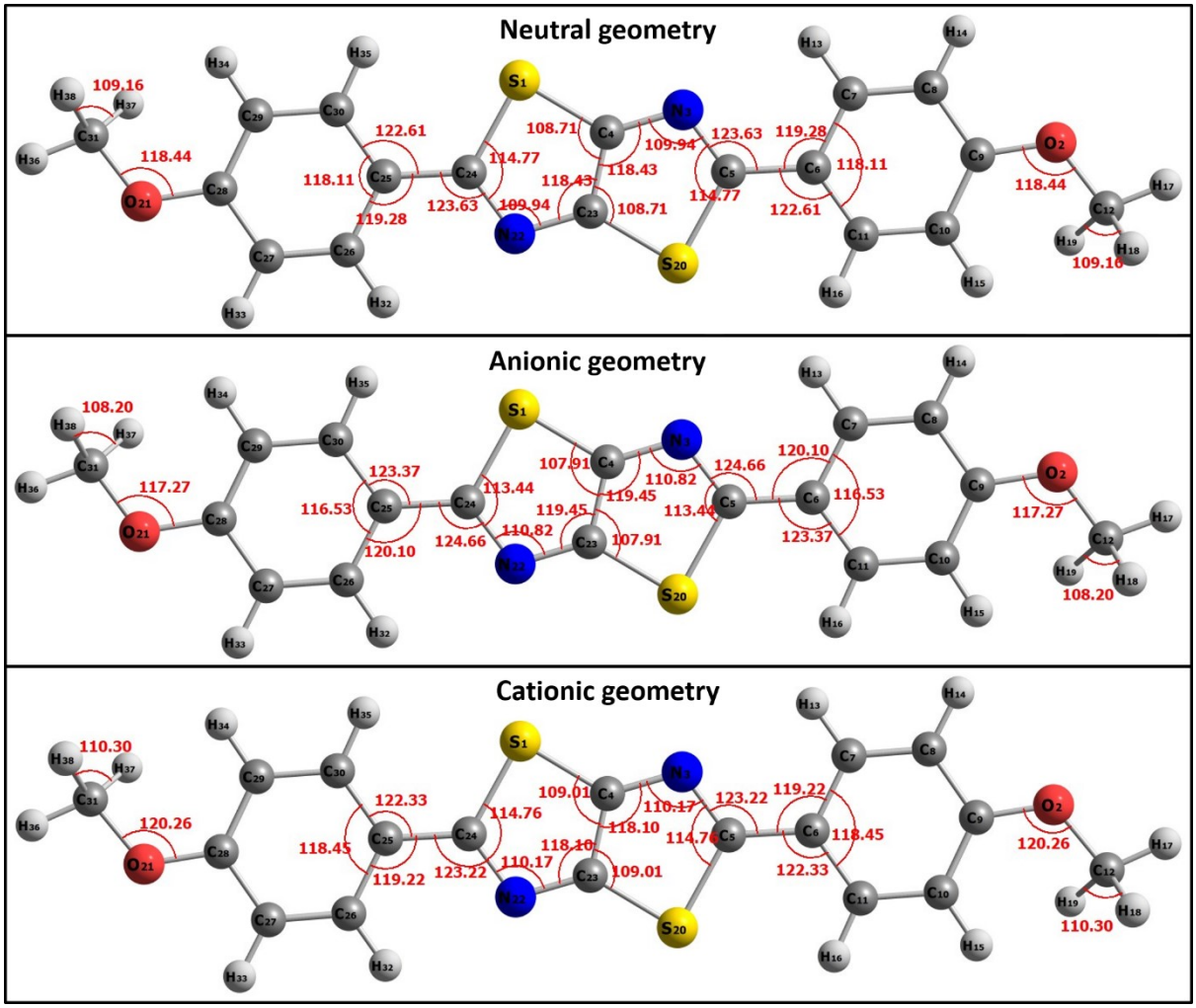

Fig. S5 Calculated bond angles, in degree, of MOP-TZTZ in optimized neutral, anionic, and cationic geometries for selected atomic specifications.

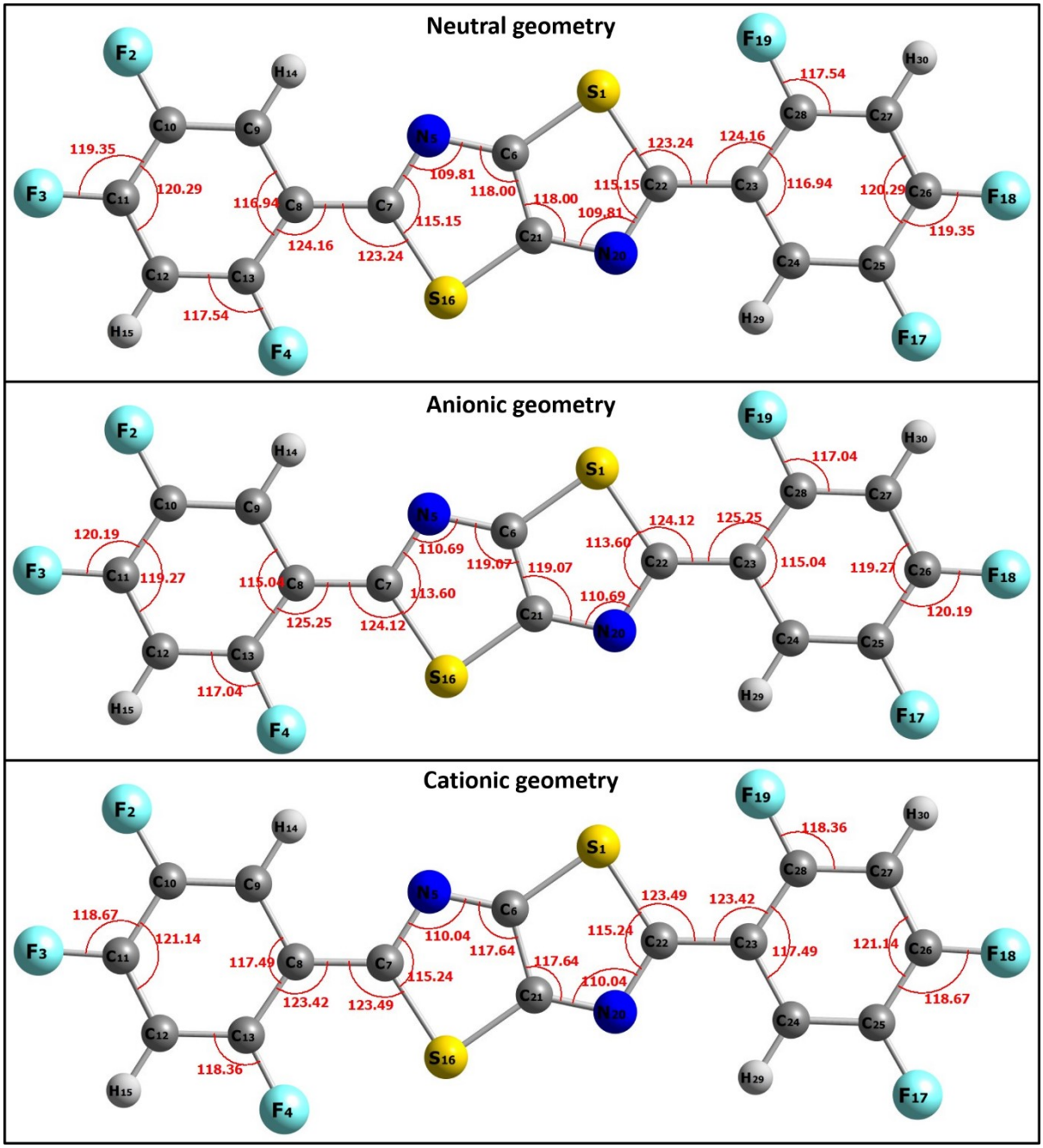

Fig. S6 Calculated bond angles, in degree, of TFP-TZTZ in optimized neutral, anionic, and cationic geometries for selected atomic specifications.

Molecule	Atomic specification	Torsion angle (degree)		
		Neutral	Anionic	Cationic
MOP-TZTZ	N3-C5-C6-C7	-0.5963	-0.0888	-0.125
	N3-C5-C6-C11	179.4322	179.9305	179.9255
	S20-C5-C6-C7	179.2807	179.8286	179.7905
	S20-C5-C6-C11	-0.6908	-0.1522	-0.1591
	S1-C24-C25-C26	-179.2807	-179.8286	-179.7905
	S1-C24-C25-C30	0.6908	0.1522	0.1591
	N22-C24-C25-C26	0.5963	0.0888	0.125
	N22-C24-C25-C30	-179.4322	-179.9305	-179.9255
TFP-TZTZ	N5-C7-C8-C9	-0.1594	-0.0719	-0.0661
	N5-C7-C8-C13	179.8739	179.9556	-179.9985
	S16-C7-C8-C9	179.741	179.803	179.8536
	S16-C7-C8-C13	-0.2258	-0.1695	-0.0788
	S1-C22-C23-C24	-179.741	-179.803	-179.8536
	S1-C22-C23-C28	0.2258	0.1695	0.0788
	N20-C22-C23-C24	0.1594	0.0719	0.0661
	N20-C22-C23-C28	-179.8739	-179.9556	179.9985

Table S1 Calculated dihedral angles of the studied molecules in optimized neutral, anionic, and cationic geometries for selected atomic specifications.

Molecule	Pair	Intermolecular distance (Å)	Electronic coupling ($x10^{-3}$ eV)		Spatial overlap integral ($x10^{-4}$)		i^{th} Site energy (eV)		j^{th} Site energy (eV)		Site energy difference (eV)	
			Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron
MOP-TZTZ	13	10.69	-2.860	-6.509	2.957	9.086	-4.756	-2.416	-5.147	-2.827	-0.391	-0.411
	14	10.69	-2.871	-6.554	2.956	9.124	-5.147	-2.827	-4.756	-2.416	0.391	0.411
	23	10.69	-2.873	-6.538	2.956	9.127	-5.147	-2.827	-4.756	-2.416	0.391	0.411
	24	10.69	-2.855	-6.526	2.956	9.135	-4.756	-2.416	-5.147	-2.827	-0.391	-0.411
	34	18.56	-4.493	1.371	4.136	-1.751	-4.970	-2.618	-4.970	-2.618	0.000	0.000
TFP-TZTZ	13	6.07	-5.705	22.216	4.383	-33.325	-5.860	-3.362	-5.860	-3.362	0.000	0.000
	23	17.14	-1.786	-0.194	1.396	-0.068	-5.826	-3.320	-5.826	-3.320	0.000	0.000
	34	15.84	-14.182	2.447	10.355	-1.614	-5.871	-3.363	-5.871	-3.363	0.000	0.000
	35	6.83	2.193	-5.337	-1.936	11.110	-5.881	-3.373	-5.881	-3.373	0.000	0.000
	37	3.74	99.023	31.146	-80.518	-51.781	-5.835	-3.336	-5.835	-3.336	0.000	0.000
	47	16.71	1.222	0.820	-0.694	-0.451	-5.886	-3.377	-5.886	-3.377	0.000	0.000

Table S2 Calculated electronic coupling (or) charge transfer integral, spatial overlap integral, i^{th} and j^{th} sites energy and their difference in different molecular pairs of the studied molecular solids.

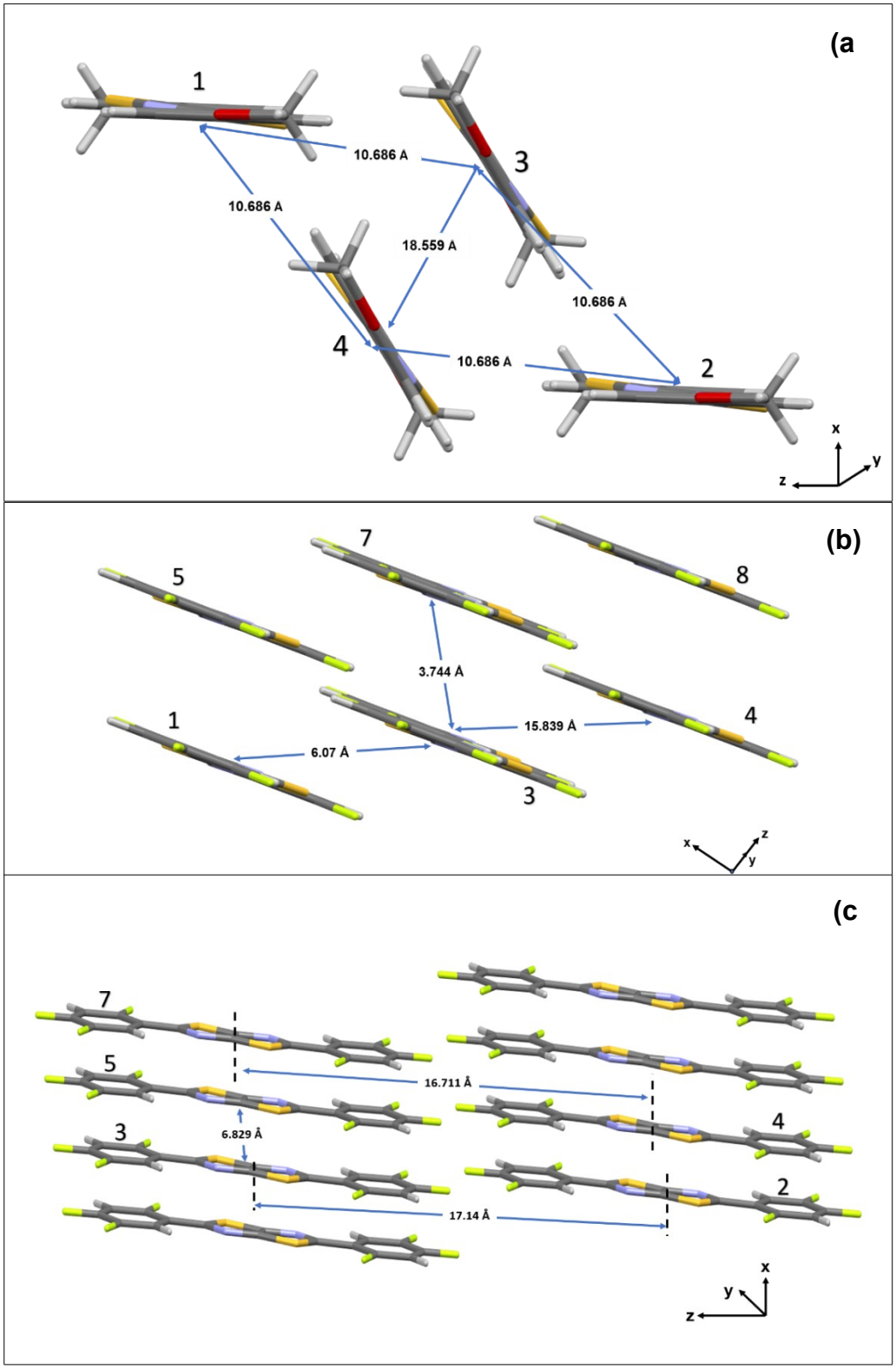

Fig. S7 Crystal structure with possible charge transport pathways and their intermolecular distances of molecular crystal MOP-TZTZ (a) and molecular crystal TFP-TZTZ in x-y plane view (b) and long molecular axis view (c)

MOP-TZTZ											
Charge	Assigned site energy difference (meV)	Pair 13		Pair 14		Pair 23		Pair 24		Pair 34	
		W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-10} s)
Hole	0	1.326	7.52	1.347	7.40	1.352	7.37	1.318	7.56	4.044	2.46
	15	1.762	5.66	1.790	5.57	1.797	5.55	1.752	5.69	5.374	1.85
	30	2.315	4.30	2.352	4.24	2.361	4.22	2.301	4.33	7.061	1.41
	45	3.008	3.31	3.056	3.26	3.066	3.25	2.990	3.33	9.172	1.09
	60	3.863	2.58	3.924	2.54	3.938	2.53	3.839	2.60	11.778	0.85
	75	4.904	2.03	4.982	2.00	5.000	1.99	4.874	2.04	14.954	0.67
	90	6.156	1.62	6.254	1.59	6.276	1.59	6.118	1.63	18.771	0.53

Table S3 Calculated rate coefficient and drift time for hole transport at different electric field-assisted site energy gap values in different molecular pairs of MOP-TZTZ.

MOP-TZTZ											
Charge	Assigned site energy difference (meV)	Pair 13		Pair 14		Pair 23		Pair 24		Pair 34	
		W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-10} s)
Electron	0	2.834	3.52	2.883	3.46	2.860	3.49	2.841	3.51	0.139	7.19
	15	3.761	2.65	3.826	2.61	3.795	2.63	3.769	2.64	0.184	5.42
	30	4.919	2.03	5.004	1.99	4.963	2.01	4.930	2.02	0.241	4.14
	45	6.341	1.57	6.450	1.55	6.398	1.56	6.355	1.57	0.310	3.21
	60	8.057	1.24	8.196	1.22	8.129	1.23	8.075	1.23	0.394	2.53
	75	10.090	0.99	10.264	0.97	10.180	0.98	10.113	0.99	0.493	2.02
	90	12.455	0.80	12.670	0.79	12.566	0.79	12.483	0.80	0.609	1.64

Table S4 Calculated rate coefficient and drift time for electron transport at different electric field-assisted site energy gap values in different molecular pairs of MOP-TZTZ.

TFP-TZTZ													
Charge	Assigned site energy difference (meV)	Pair 13		Pair 23		Pair 34		Pair 35		Pair 37		Pair 47	
		W (10^9 s^{-1})	t_d (10^{-11} s)	W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-12} s)	W (10^9 s^{-1})	t_d (10^{-10} s)	W (10^9 s^{-1})	t_d (10^{-13} s)	W (10^9 s^{-1})	t_d (10^{-9} s)
Hole	0	8.630	11.55	0.829	12.02	57.594	17.31	0.976	10.22	2375.65	4.20	0.580	17.18
	15	11.465	8.69	1.101	9.05	76.513	13.03	1.296	7.69	3156.01	3.16	0.771	12.93
	30	15.047	6.62	1.445	6.90	100.418	9.93	1.701	5.86	4142.05	2.41	1.012	9.85
	45	19.510	5.11	1.874	5.32	130.200	7.66	2.206	4.52	5370.51	1.86	1.312	7.60
	60	24.990	3.99	2.401	4.15	166.775	5.98	2.825	3.53	6879.18	1.45	1.680	5.93
	75	31.624	3.15	3.038	3.28	211.045	4.72	3.575	2.79	8705.23	1.14	2.126	4.69
	90	39.535	2.52	3.798	2.62	263.840	3.78	4.470	2.23	10882.92	0.92	2.658	3.75

Table S5 Calculated rate coefficient and drift time for hole transport at different electric field-assisted site energy gap values in different molecular pairs of TFP-TZTZ.

TFP-TZTZ													
Charge	Assigned site energy difference (meV)	Pair 13		Pair 23		Pair 34		Pair 35		Pair 37		Pair 47	
		W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-9} s)	W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-11} s)	W (10^{10} s^{-1})	t_d (10^{-12} s)	W (10^{10} s^{-1})	t_d (10^{-10}s)
Electron	0	16.746	11.55	0.006	15.41	0.501	19.90	0.349	28.56	26.575	3.75	0.062	16.18
	15	22.230	8.69	0.009	11.61	0.665	14.99	0.463	21.51	35.277	2.83	0.082	12.19
	30	29.107	6.62	0.011	8.87	0.870	11.45	0.607	16.43	46.190	2.16	0.107	9.31
	45	37.593	5.11	0.015	6.87	1.124	8.87	0.783	12.72	59.656	1.67	0.138	7.21
	60	47.892	3.99	0.018	5.39	1.432	6.96	0.998	9.99	75.999	1.31	0.176	5.66
	75	60.181	3.15	0.023	4.29	1.800	5.54	1.254	7.95	95.501	1.04	0.221	4.50
	90	74.593	2.52	0.029	3.46	2.231	4.47	1.555	6.41	118.372	0.84	0.274	3.63

Table S6 Calculated rate coefficient and drift time for electron transport at different electric field-assisted site energy gap values in different molecular pairs of TFP-TZTZ.

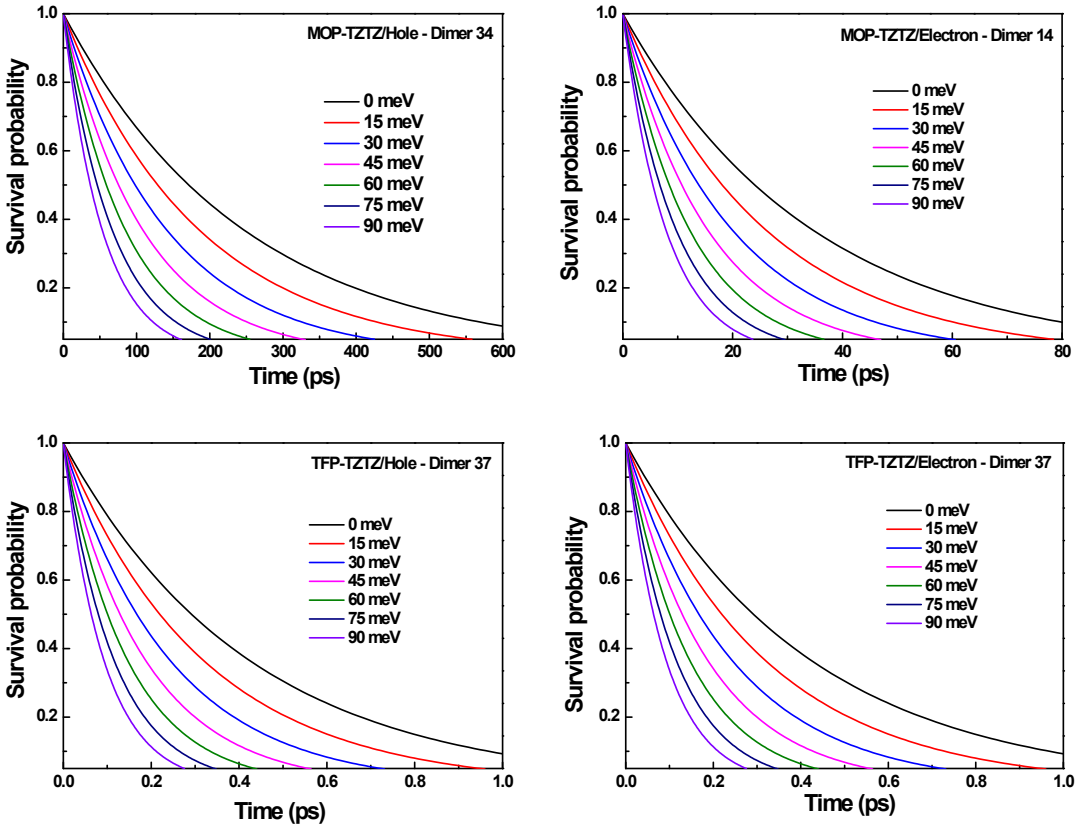

Fig. S8 Survival probability analysis for hole and electron transport in different pairs (dimer) of the studied molecules at different electric field coupled site energy difference values.

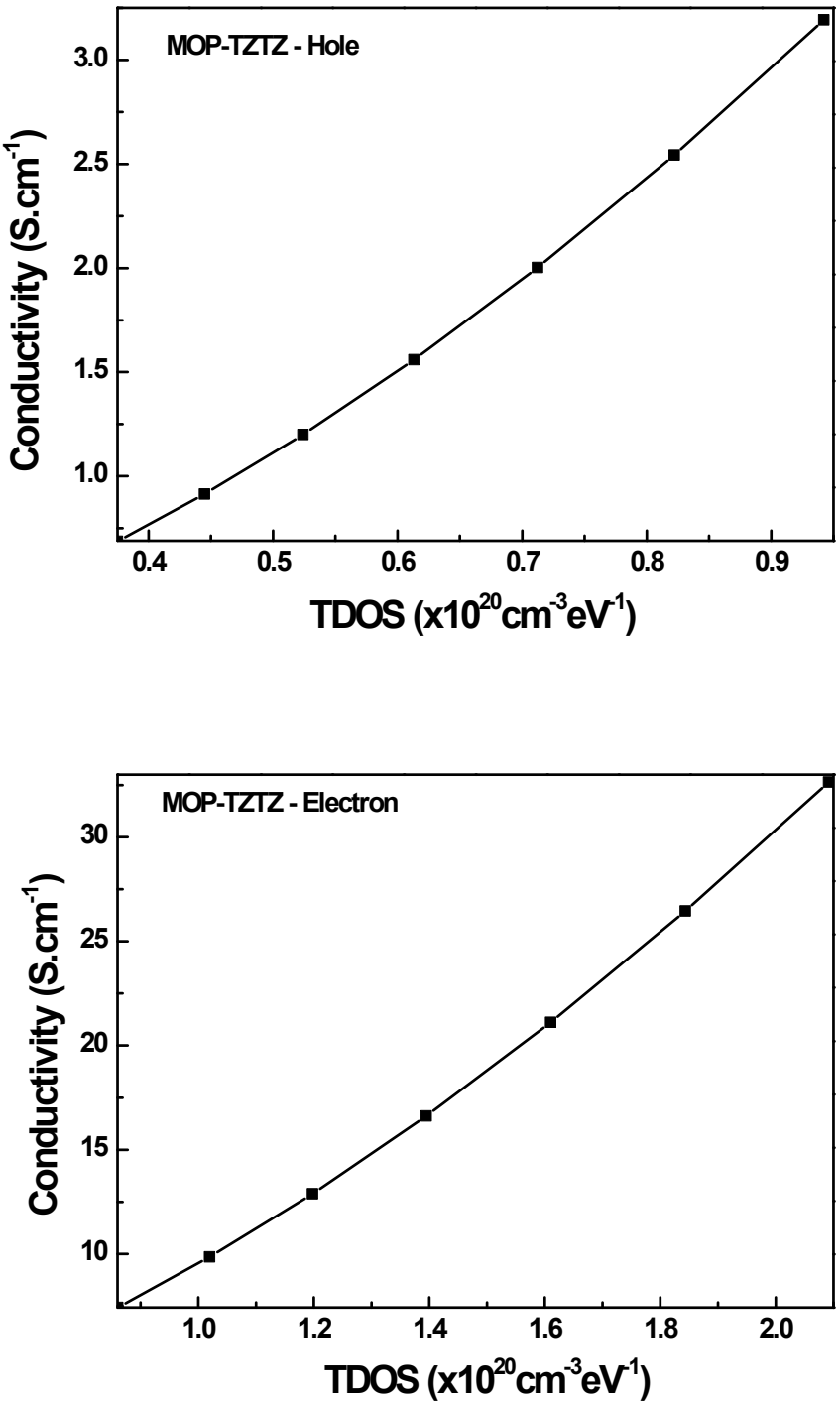

Fig. S9 Plot of change in conductivity with respect to thermodynamic density of states (TDOS) for hole and electron transport in MOP-TZTZ.

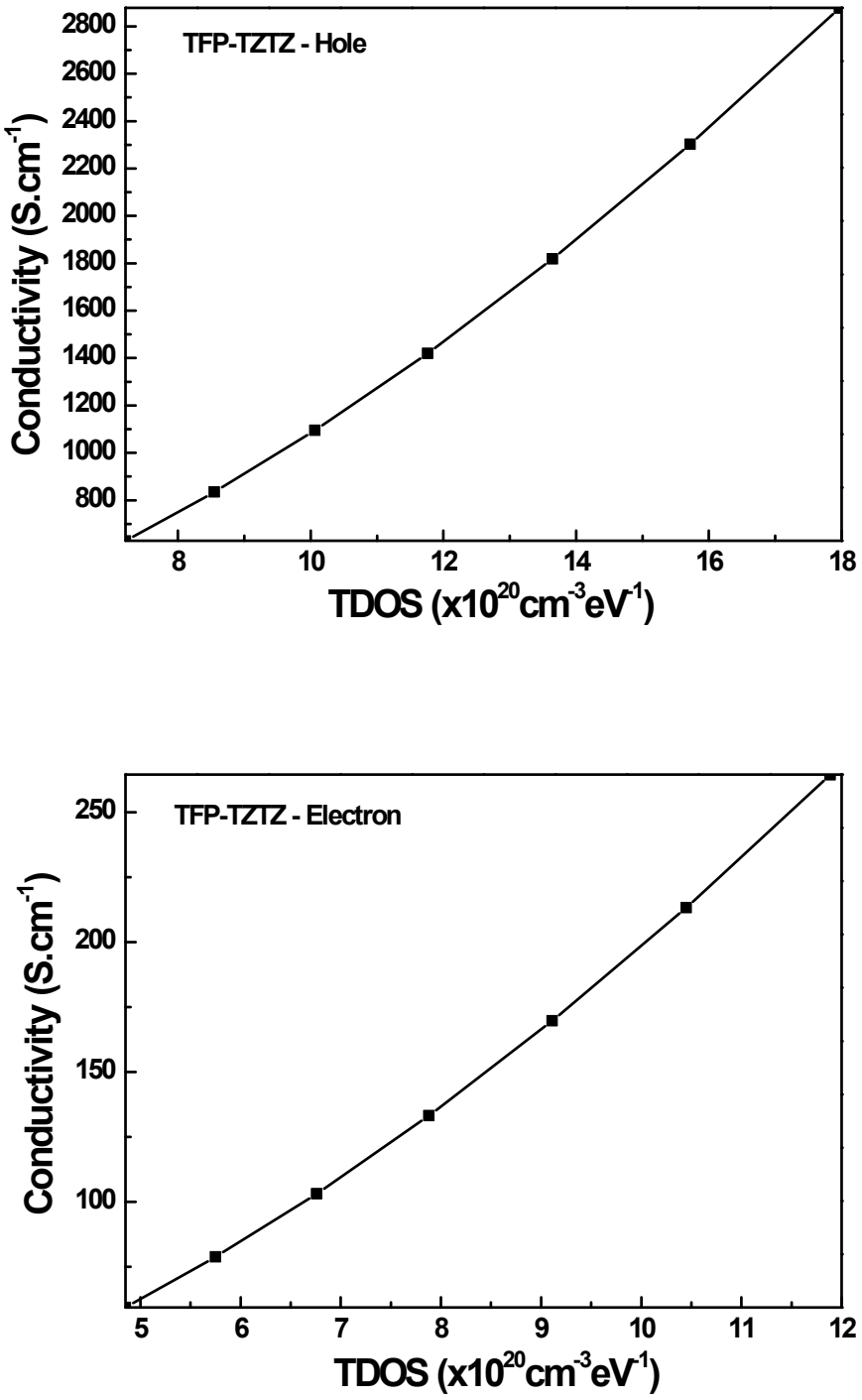

Fig. S10 Plot of change in conductivity with respect to thermodynamic density of states (TDOS) for hole and electron transport in TFP-TZTZ.

Molecule	$\Delta\eta/\Delta h_s$ (meV)	Entropy-ruled D/μ ratio (mV)	Enhancement factor
MOP-TZTZ - Hole	48.22	80.367	3.103
MOP-TZTZ -Electron	50.33	83.883	3.239
TFP-TZTZ - Hole	48.72	81.200	3.135
TFP-TZTZ - Electron	49.8	83	3.205

Table S7 Calculated $\Delta\eta/\Delta h_s$ value, entropy-ruled D/μ ratio, and enhancement factor for the studied molecular solids.

Molecule	$\Delta E_{ij}(\vec{E})$ (meV)	TDOS (x10^{20} $cm^3 \cdot eV)^{-1}$	Conductivity (S/cm)	Ideality factor
MOP-TZTZ Hole	0	0.375	0.69	1.028
	15	0.445	0.91	
	30	0.524	1.20	
	45	0.613	1.56	
	60	0.712	2.00	
	75	0.822	2.54	
	90	0.942	3.19	
MOP-TZTZ Electron	0	0.860	7.43	0.939
	15	1.020	9.86	
	30	1.198	12.89	
	45	1.395	16.62	
	60	1.610	21.12	
	75	1.843	26.45	
	90	2.091	32.65	
TFP-TZTZ Hole	0	7.210	628.09	1.001
	15	8.550	834.42	
	30	10.065	1095.09	
	45	11.763	1419.94	
	60	13.646	1818.68	
	75	15.717	2301.65	
	90	17.969	2877.36	
TFP-TZTZ Electron	0	4.851	59.36	0.956
	15	5.750	78.79	
	30	6.759	103.17	
	45	7.880	133.24	
	60	9.112	169.75	
	75	10.451	213.30	
	90	11.888	264.39	

Table S8 Different $\Delta E(\vec{E})$ assisted TDOS, conductivity, and ideality factor for the studied molecular solids.

Molecule	Pair	Intermolecular distance (Å)	Hole mobility ($x10^{-4}$ cm^2/Vs)	Electron mobility ($x10^{-2}$ cm^2/Vs)
MOP-TZTZ	13	10.69	5.858	1.252
	14	10.69	5.951	1.274
	23	10.69	5.972	1.263
	24	10.69	5.822	1.255
	34	18.56	53.875	0.185
TFP-TZTZ	13	6.07	12.300	2.387
	23	17.14	9.422	0.007
	34	15.84	558.976	0.486
	35	6.83	1.761	0.063
	37	3.74	1288.132	1.441
	47	16.71	6.267	0.067

Table S9 For comparative study (for making comparison between the Entropy-ruled mobility and Einstein's mobility), the calculated hole and electron mobility using conventional Einstein's relation ($\mu = qD/k_BT$) in different pairs of the studied molecular solids is presented.

Molecule	$\Delta E_{ij}(\vec{E})$ (meV)	Total current density between different pairs of MOP-TZTZ (mA/cm^2)				
		Pair 13	Pair 14	Pair 23	Pair 24	Pair 34
MOP-TZTZ/Hole	0	63.23	63.23	63.23	63.23	109.81
	15	77.90	77.90	77.90	77.90	135.29
	30	94.84	94.84	94.84	94.84	164.70
	45	114.20	114.20	114.20	114.20	198.34
	60	136.16	136.16	136.16	136.16	236.46
	75	160.84	160.84	160.84	160.84	279.33
	90	188.36	188.36	188.36	188.36	327.12
MOP-TZTZ/Electron	0	94.42	94.42	94.42	94.42	163.97
	15	118.36	118.36	118.36	118.36	205.56
	30	146.02	146.02	146.02	146.02	253.59
	45	177.59	177.59	177.59	177.59	308.42
	60	213.22	213.22	213.22	213.22	370.29
	75	252.98	252.98	252.98	252.98	439.34
	90	296.87	296.87	296.87	296.87	515.56

Table S10 Calculated total current density for hole and electron transport in different pairs of MOP-TZTZ molecular solid.

Molecule	$\Delta E_{ij}(\vec{E})$ (meV)	Total current density between different pairs of TFP-TZTZ (mA/cm^2)					
		Pair 13	Pair 23	pair 34	pair 35	pair 37	Pair 47
TFP-TZTZ/Hole	0	247.24	698.15	645.19	278.19	152.50	680.66
	15	305.96	863.96	798.42	344.26	188.72	842.31
	30	373.73	1055.34	975.28	420.52	230.52	1028.90
	45	451.24	1274.19	1177.53	507.73	278.32	1242.27
	60	538.98	1521.96	1406.50	606.46	332.45	1483.84
	75	637.50	1800.17	1663.60	717.32	393.22	1755.07
	90	747.05	2109.49	1949.46	840.58	460.78	2056.64
TFP-TZTZ/Electron	0	175.62	495.91	458.29	197.61	108.32	483.49
	15	219.26	619.14	572.17	246.71	135.24	603.63
	30	269.66	761.45	703.68	303.42	166.32	742.37
	45	327.22	923.99	853.89	368.18	201.83	900.84
	60	392.26	1107.64	1023.61	441.36	241.94	1079.89
	75	464.97	1312.97	1213.36	523.18	286.79	1280.07
	90	545.45	1540.23	1423.38	613.74	336.44	1501.64

Table S11 Calculated total current density for hole and electron transport in different pairs of TFP-TZTZ molecular solid.

Molecule	$\Delta E_{ij}(\vec{E})$ (meV)	ln$J$				
		Pair 13	Pair 14	Pair 23	Pair 24	Pair 34
MOP-TZTZ/Hole	0	6.45	6.45	6.45	6.45	7.00
	15	6.66	6.66	6.66	6.66	7.21
	30	6.85	6.85	6.85	6.85	7.41
	45	7.04	7.04	7.04	7.04	7.59
	60	7.22	7.22	7.22	7.22	7.77
	75	7.38	7.38	7.38	7.38	7.93
	90	7.54	7.54	7.54	7.54	8.09
MOP-TZTZ/Electron	0	6.85	6.85	6.85	6.85	7.40
	15	7.08	7.08	7.08	7.08	7.63
	30	7.29	7.29	7.29	7.29	7.84
	45	7.48	7.48	7.48	7.48	8.03
	60	7.66	7.66	7.66	7.66	8.22
	75	7.84	7.84	7.84	7.84	8.39
	90	8.00	8.00	8.00	8.00	8.55

Table S12 Calculated logarithmic total current density values for hole and electron transport in different pairs of MOP-TZTZ molecular solid.

Molecule	$\Delta E_{ij}(\vec{E})$ (meV)	ln$J$					
		Pair 13	Pair 23	pair 34	pair 35	pair 37	Pair 47
TFP-TZTZ/Hole	0	7.81	8.85	8.77	7.93	7.33	8.83
	15	8.03	9.06	8.99	8.14	7.54	9.04
	30	8.23	9.26	9.19	8.34	7.74	9.24
	45	8.41	9.45	9.37	8.53	7.93	9.43
	60	8.59	9.63	9.55	8.71	8.11	9.60
	75	8.76	9.80	9.72	8.88	8.28	9.77
	90	8.92	9.96	9.88	9.04	8.44	9.93
TFP-TZTZ/Electron	0	7.47	8.51	8.43	7.59	6.99	8.48
	15	7.69	8.73	8.65	7.81	7.21	8.71
	30	7.90	8.94	8.86	8.02	7.42	8.91
	45	8.09	9.13	9.05	8.21	7.61	9.11
	60	8.27	9.31	9.23	8.39	7.79	9.29
	75	8.44	9.48	9.40	8.56	7.96	9.46
	90	8.60	9.64	9.56	8.72	8.12	9.62

Table S13 Calculated logarithmic total current density values for hole and electron transport in different pairs of TFP-TZTZ molecular solid.