Computational study of electron transport in halogen incorporated diindenotetracene: crystal structure, charge transport and optoelectronic properties

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Table S1: The optimized structure and their space group and structural parameters of DIT derivatives are listed in the table.

Compounds	Optimized Structure	Space group	Structural parameters
DIT		C2/c	a=24.802 Å, b=3.8834 Å, c=21.100 Å α=90°, β=119.40°, γ= 90°
DIT-F		<i>P</i> 2 ₁	a= 13.7824 Å, b=25.3815 Å, c= 3.8992 Å α=90°, β=69.27°, γ=90°
DIT-Cl		<i>P</i> 1	a= 3.9510 Å, b= 13.7389 Å, c= 13.9925 Å α= 87.34°, β= 74.86°, γ= 79.33°
DIT-Br		<i>P</i> 1	a= 15.3681 Å, b= 3.9502 Å, c= 15.2183 Å α= 96.67°, β= 102.76°, γ= 104.76°

DIT-I	<i>P</i> 1	a= 8.6662 Å, b= 16.2511 Å, c= 11.5107 Å α = 90.01°, β = 117.70°, γ = 92.70°

 Table S2 (a): Bond length of the neutral and charged states of DIT compound.

Bond Index	neutral (exp.) ¹ (Å)	anion (Å)	cation (Å)	anion-neutral	cation-neutral
1	1.39094 (1.40774)	1.39869	1.38305	0.00775	-0.00789
2	1.40110 (1.35014)	1.39721	1.40970	-0.00389	0.0086
3	1.38904 (1.42250)	1.39695	1.38310	0.00791	-0.00594
4	1.48056 (1.41809)	1.46125	1.48328	-0.01931	0.00272
5	1.41078 (1.47909)	1.43124	1.42429	0.02046	0.01351
6	1.42793 (1.38217)	1.41785	1.41541	-0.01008	-0.01252
7	1.36753 (1.38909)	1.38086	1.37915	0.01333	0.01162
8	1.42110 (1.37427)	1.40783	1.40741	-0.01327	-0.01369
9	1.36753 (1.38208)	1.38086	1.37915	0.01333	0.01162
10	1.42793 (1.39084)	1.41785	1.41541	-0.01008	-0.01252
11	1.41078 (1.47604)	1.43124	1.42429	0.02046	0.01351
12	1.44168 (1.46268)	1.45728	1.43900	0.0156	-0.00268
13	1.40051 (1.39648)	1.40277	1.39820	0.00226	-0.00231
14	1.48111 (1.43910)	1.47255	1.47400	-0.00856	-0.00711
15	1.40110 (1.35013)	1.39721	1.40970	-0.00389	0.0086
16	1.38904 (1.43475)	1.39695	1.38310	0.00791	-0.00594
17	1.48056 (1.40027)	1.46125	1.48328	-0.01931	0.00272
18	1.40051 (1.41141)	1.40277	1.39820	0.00226	-0.00231
19	1.37868 (1.36219)	1.38421	1.37984	0.00553	0.00116
20	1.40051 (1.41141)	1.40277	1.39820	0.00226	-0.00231

Table S2 (b): Bond length of the neutral and charge states of DIT-F compound.

Bond Index	neutral (Å)	anion (Å)	cation (Å)	anion-neutral	cation-neutral
1	1.38717	1.39048	1.39525	0.00331	0.00808
2	1.39184	1.38657	1.38604	-0.00527	-0.0058
3	1.38866	1.39674	1.39666	0.00808	0.008
4	1.47807	1.45889	1.45578	-0.01918	-0.02229
5	1.40878	1.42882	1.42950	0.02004	0.02072
6	1.42685	1.41723	1.41091	-0.00962	-0.01594
7	1.35865	1.37058	1.37463	0.01193	0.01598
8	1.41899	1.39994	1.40662	-0.01905	-0.01237
9	1.35865	1.37058	1.37463	0.01193	0.01598

10	1.42685	1.41723	1.41091	-0.00962	-0.01594
11	1.40878	1.42882	1.42950	0.02004	0.02072
12	1.44144	1.45634	1.44760	0.0149	0.00616
13	1.40050	1.40212	1.41697	0.00162	0.01647
14	1.48277	1.47302	1.47055	-0.00975	-0.01222
15	1.39184	1.38657	1.38604	-0.00527	-0.0058
16	1.38866	1.39674	1.39666	0.00808	0.008
17	1.47807	1.45889	1.45578	-0.01918	-0.02229
18	1.40050	1.40212	1.39186	0.00162	-0.00864
19	1.37643	1.38225	1.36956	0.00582	-0.00687
20	1.40050	1.40212	1.41697	0.00162	0.01647

 Table S2 (c): Bond length of the neutral and charge states of DIT-Cl compound.

Bond Index	neutral (Å)	anion (Å)	cation (Å)	anion-neutral	cation-neutral
1	1.39594	1.40014	1.39278	0.0042	-0.00316
2	1.40176	1.39533	1.41120	-0.00643	0.00944
3	1.38464	1.39247	1.37943	0.00783	-0.00521
4	1.47743	1.45885	1.47882	-0.01858	0.00139
5	1.41018	1.42917	1.42326	0.01899	0.01308
6	1.42316	1.41345	1.41072	-0.00971	-0.01244
7	1.36692	1.37841	1.38040	0.01149	0.01348
8	1.43041	1.41035	1.42141	-0.02006	-0.009
9	1.36692	1.37841	1.38040	0.01149	0.01348
10	1.42316	1.41345	1.41072	-0.00971	-0.01244
11	1.41018	1.42917	1.42326	0.01899	0.01308
12	1.44036	1.45394	1.43891	0.01358	-0.00145
13	1.40078	1.40219	1.39890	0.00141	-0.00188
14	1.47697	1.46873	1.47104	-0.00824	-0.00593
15	1.40176	1.39533	1.41134	-0.00643	0.00958
16	1.38464	1.39247	1.37918	0.00783	-0.00546
17	1.47743	1.45885	1.47931	-0.01858	0.00188
18	1.40078	1.40219	1.39824	0.00141	-0.00254
19	1.37809	1.38345	1.37978	0.00536	0.00169
20	1.40078	1.40219	1.39890	0.00141	-0.00188

 Table S2 (d): Bond length of the neutral and charge states of DIT-Br compound.

Bond Index	neutral (Å)	anion (Å)	cation (Å)	anion-neutral	cation-neutral
1	1.39277	1.39632	1.38915	0.00355	-0.00362
2	1.40130	1.39492	1.41130	-0.00638	0.01
3	1.38479	1.39261	1.37940	0.00782	-0.00539
4	1.47737	1.45894	1.47856	-0.01843	0.00119

5	1.40999	1.42850	1.42276	0.01851	0.01277
6	1.42373	1.41418	1.41128	-0.00955	-0.01245
7	1.36624	1.37736	1.38009	0.01112	0.01385
8	1.42722	1.40714	1.41798	-0.02008	-0.00924
9	1.36624	1.37736	1.38009	0.01112	0.01385
10	1.42373	1.41418	1.41128	-0.00955	-0.01245
11	1.40999	1.42850	1.42276	0.01851	0.01277
12	1.43910	1.45226	1.43778	0.01316	-0.00132
13	1.40069	1.40216	1.39879	0.00147	-0.0019
14	1.47551	1.46732	1.46955	-0.00819	-0.00596
15	1.40130	1.39492	1.41130	-0.00638	0.01
16	1.38479	1.39261	1.37940	0.00782	-0.00539
17	1.47737	1.45894	1.47856	-0.01843	0.00119
18	1.40069	1.40216	1.39879	0.00147	-0.0019
19	1.37822	1.38345	1.37974	0.00523	0.00152
20	1.40069	1.40216	1.39879	0.00147	-0.0019

 Table S2 (e): Bond length of the neutral and charge states of DIT-I compound.

Bond Index	neutral (Å)	anion (Å)	cation (Å)	anion-neutral	cation-neutral
1	1.39664	1.40048	1.39343	0.00384	-0.00321
2	1.40555	1.39915	1.41511	-0.0064	0.00956
3	1.38460	1.39202	1.37930	0.00742	-0.0053
4	1.47761	1.45902	1.47813	-0.01859	0.00052
5	1.41050	1.42940	1.42255	0.0189	0.01205
6	1.42361	1.41358	1.41150	-0.01003	-0.01211
7	1.36993	1.38164	1.38325	0.01171	0.01332
8	1.43166	1.41124	1.42316	-0.02042	-0.0085
9	1.36993	1.38164	1.38325	0.01171	0.01332
10	1.42361	1.41358	1.41150	-0.01003	-0.01211
11	1.41050	1.42940	1.42255	0.0189	0.01205
12	1.43795	1.45154	1.43713	0.01359	-0.00082
13	1.40083	1.40228	1.39915	0.00145	-0.00168
14	1.47337	1.46543	1.46782	-0.00794	-0.00555
15	1.40555	1.39915	1.41511	-0.0064	0.00956
16	1.38460	1.39202	1.37930	0.00742	-0.0053
17	1.47761	1.45902	1.47813	-0.01859	0.00052
18	1.40083	1.40228	1.39915	0.00145	-0.00168
19	1.37853	1.38370	1.38015	0.00517	0.00162
20	1.40083	1.40228	1.39915	0.00145	-0.00168

compounds	neutral (exp.) ^[1] (°)	anion (°)	cation (°)
DIT	$\theta 1 = 120.589 (120.750)$	$\theta 1 = 120.544 \ \theta 2 = 120.544$	$\theta 1 = 120.580 \ \theta 2 = 120.589$
	θ2=120.589 (120.410)	$\theta 3 = 119.927 \ \theta 4 = 119.927$	$\theta 3 = 120.322 \ \theta 4 = 120.322$
	$\theta 3 = 120.399 (121.378)$	$\theta 5 = 120.544 \ \theta 6 = 120.544$	$\theta 5 = 120.580 \ \theta 6 = 120.589$
	θ4=120.399 (120.393)	$\theta 7 = 119.927 \ \theta 8 = 119.927$	$\theta 7 = 120.322 \ \theta 8 = 120.322$
	$\theta 5 = 120.589 (120.750)$		
	θ6=120.589 (120.410)		
	θ 7=120.399 (121.378)		
	θ8=120.399 (120.393)		
DIT-F	$\theta 1 = 121.104 \ \theta 2 = 121.104$	$\theta 1 = 121.251 \ \theta 2 = 121.251$	$\theta 1 = 121.601 \ \theta 2 = 120.681$
	$\theta 3 = 121.016 \ \theta 4 = 121.016$	$\theta 3 = 120.663 \ \theta 4 = 120.663$	$\theta 3 = 120.582 \ \theta 4 = 120.582$
	$\theta 5 = 121.104 \ \theta 6 = 121.104$	$\theta 5 = 121.251 \ \theta 6 = 121.251$	$\theta 5 = 120.681 \ \theta 6 = 121.601$
	θ 7=121.016 θ 8=121.016	θ 7=120.663 θ 8=120.663	$\theta 7 = 121.006 \ \theta 8 = 121.006$
DIT-Cl	$\theta 1 = 120.325 \ \theta 2 = 120.325$	$\theta 1 = 120.490 \ \theta 2 = 120.490$	$\theta 1 = 120.142 \ \theta 2 = 120.133$
	$\theta 3 = 120.022 \ \theta 4 = 120.022$	$\theta 3 = 119.830 \ \theta 4 = 119.830$	$\theta 3 = 119.744 \ \theta 4 = 119.744$
	$\theta 5 = 120.325 \ \theta 6 = 120.325$	$\theta 5 = 120.490 \ \theta 6 = 120.490$	$\theta 5 = 120.133 \ \theta 6 = 120.142$
	θ 7=120.022 θ 8=120.022	$\theta 7 = 119.830 \ \theta 8 = 119.830$	$\theta 7 = 119.750 \ \theta 8 = 119.750$
DIT-Br	$\theta 1 = 120.367 \ \theta 2 = 120.367$	$\theta 1 = 120.572 \ \theta 2 = 120.572$	$\theta 1 = 120.177 \ \theta 2 = 120.177$
	$\theta 3 = 120.052 \ \theta 4 = 120.052$	$\theta 3 = 119.904 \ \theta 4 = 119.904$	$\theta 3 = 119.763 \ \theta 4 = 119.763$
	$\theta 5 = 120.367 \ \theta 6 = 120.367$	$\theta 5 = 120.572 \ \theta 6 = 120.572$	$\theta 5 = 120.177 \ \theta 6 = 120.177$
	$\theta 7 = 120.052 \ \theta 8 = 120.052$	$\theta 7 = 119.904 \ \theta 8 = 119.904$	$\theta 7 = 119.763 \ \theta 8 = 119.763$
DIT-I	$\theta 1 = 120.069 \ \theta 2 = 120.069$	$\theta 1 = 120.272 \ \theta 2 = 120.272$	$\theta 1 = 119.867 \ \theta 2 = 119.867$
	$\theta 3 = 119.705 \ \theta 4 = 119.705$	$\theta 3 = 119.579 \ \theta 4 = 119.579$	$\theta 3 = 119.401 \ \theta 4 = 119.401$
	$\theta 5 = 120.069 \ \theta 6 = 120.069$	$\theta 5 = 120.272 \ \theta 6 = 120.272$	$\theta 5 = 119.867 \ \theta 6 = 119.867$
	$\theta 7 = 119.705 \ \theta 8 = 119.705$	$\theta 7 = 119.579 \ \theta 8 = 119.579$	$\theta 7 = 119.401 \ \theta 8 = 119.401$

Table S3: Bond angles of the DIT derivatives.

Table S4: Dihedral angles of the DIT derivatives; all the compounds are completely planner.

compounds	neutral	anion	cation
DIT	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00
	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00
DIT-F	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00
	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00
DIT-Cl	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00
	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00
DIT-Br	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00
	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00
DIT-I	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00	δ1=0.00 δ2=0.00
	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00	δ3=0.00 δ4=0.00

Compounds	НОМО	LOMO
DIT		
DIT-F		
DIT-Cl		
DIT-Br		

Table S5: Frontier molecular orbitals (HOMO and LUMO) of the studied DIT derivatives.





Fig. S1: Change in bond length with respect to bond index of the DIT derivatives; (A) oxidation state and (B) reduction state.

Charge Transfer Integral:

Charge transfer integral between the two adjacent molecules in a dimer are investigated by site energy corrected method at ω b97xd/6-31G(d,p) level in the AOMIX program [2]. It is the most reliable method to investigate the electronic coupling of the investigated systems.





Fig. S2: Crystal packing and hopping pathways of the DIT derivatives; (A) DIT (B) DIT-F (C)DIT-Cl (D) DIT-Br and (E) DIT-I.

Table S6: Frontier molecular orbitals (HOMO and LUMO) and HOMO-LUMO gap of the studied
DIT derivatives at B3LYP-D3 with different basis sets.

Basis sets	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
6-31G(d,p)	-5.093	-2.892	2.201
6-311G(d,p)	-5.345	-3.146	2.199
6-311+G(d,p)	-5.436	-3.247	2.189
6-311++G(d,p)	-5.436	-3.245	2.191

Crystal structure prediction of DIT-derivatives:

The previously optimized single molecules are used for the prediction of the organic crystals. The simulated annealing algorithm based on the Monte Carlo search process is implemented to generate the possible structures in the selected space groups such as P1, $P2_1$, $P2_12_12_1$, $P2_1/c$, Pbca, Pbcn, $Pna2_1$, C2, C2/c, and Cc, etc. We have considered clustering to remove unwanted duplicate structures after the prediction of the crystal using the selected space group [3]. This process is stochastic in nature and therefore the calculation was repeated for several times before choosing the crystal with minimum lattice energy. The cell parameters and cell volume of the experimental structure and predicted structure using Dreiding and COMPASS forcefields are given below.

Table S7: Comparison between experimental, and theoretically predicted crystal structure parameters using Dreiding and COMPASS forcefield.

Methods	Cell Parameters
Experimental	a=24.802 Å, $b=3.8834$ Å, $c=21.100$ Å $\alpha=90^{\circ}$, $\beta=119.40^{\circ}$, $\gamma=90^{\circ}$ Volume=1770.54
Theoretical (Dreiding forcefield)	<i>a</i> =21.4729 Å, <i>b</i> =3.7264 Å, <i>c</i> =25.8575 Å α=90°, β=121.135°, γ=90° Volume=1770.98
Theoretical (COMPASS forcefield)	a=22.1642, b=3.5202, c=22.8375 $\alpha=90^{\circ}, \beta=110.843^{\circ}, \gamma=90^{\circ}$ Volume=1665.23

The predicted structural parameters using the Dreiding forcefield are similar to the experimental result, whereas slightly different result is obtained using COMPASS forcefield. To verify the packing motif, we have arranged the crystal along the *bc* plane, which shows a similar arrangement as observed in experiment. The comparison between the simulated structure of bare DIT with the experimental structure as shown in the figure below.



Fig S3. Packing motif of the DIT crystal; (A) experimental and (B) theoretically predicted structure.

Hence, we used the same theoretical model to predict the crystal structures of the studied halogenated compounds, which have also been implemented in the previous reports [3-4].

References

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