

Supplementary Material

Electron – molecular vibration coupling in trimerized isostructural mixed-stack complexes (EDT-TTF-I₂)₂TCNQF_n (*n* = 0, 1, 2)

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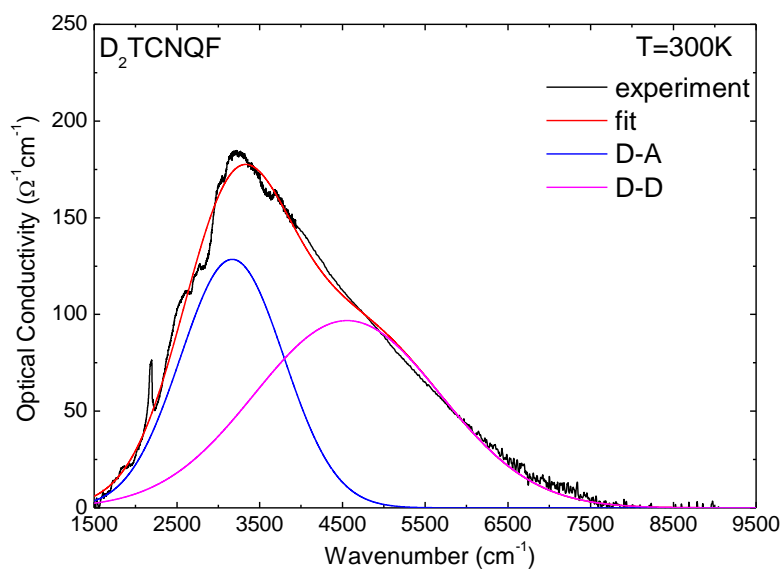


Figure S1. Deconvolution of the electronic band in IR spectrum of the D₂TCNQF complex at 300 K (polarization $E \parallel a-b$). The mid-infrared D-A band corresponds to donor-acceptor and the D-D band to donor-donor charge transfer transitions.

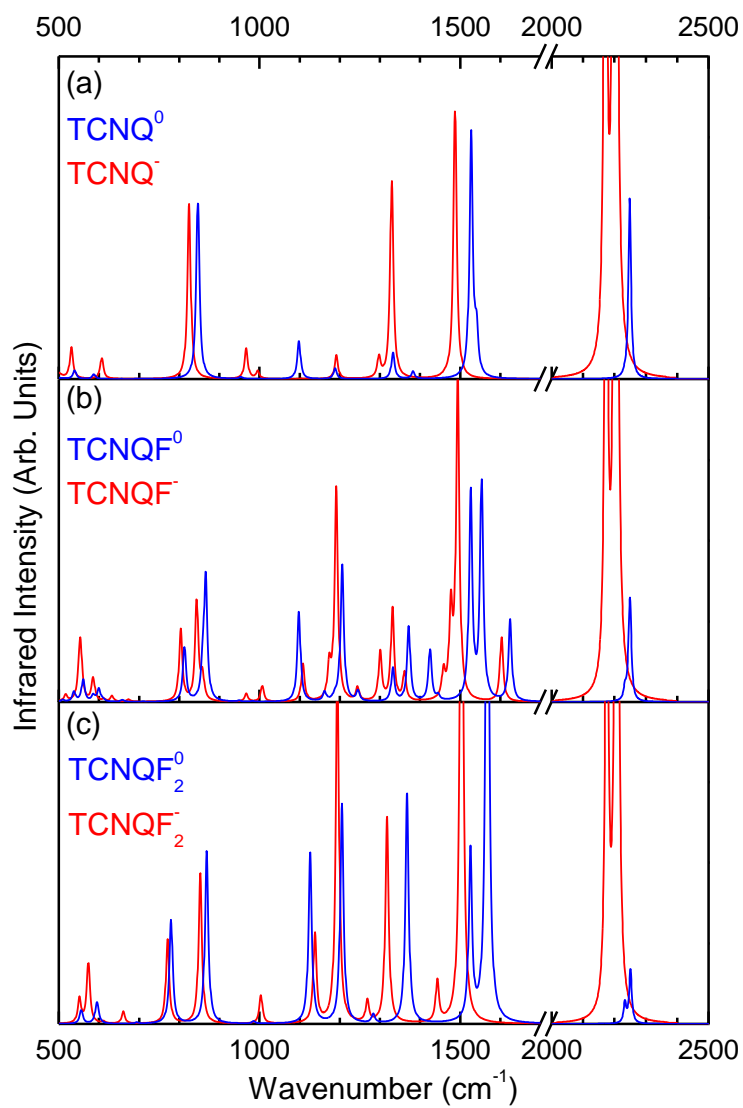


Figure S2. Theoretical infrared spectra of (a) TCNQ⁰ (blue) and TCNQ⁻ (red); (b) TCNQF⁰ (blue) and TCNQF⁻ (red); (c) TCNQF₂⁰ (blue) and TCNQF₂⁻ (red).

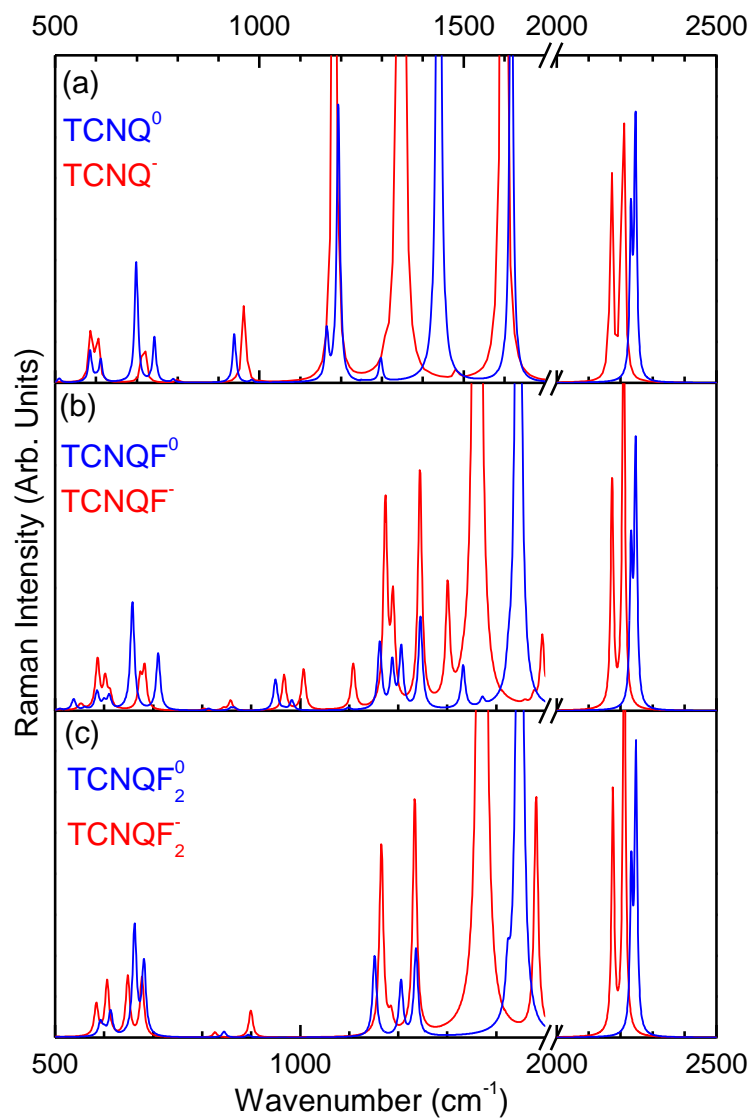


Figure S3. Theoretical Raman spectra of (a) TCNQ⁰ (blue) and TCNQ⁻ (red); (b) TCNQF⁰ (blue) and TCNQF⁻ (red); (c) TCNQF₂⁰ (blue) and TCNQF₂⁻ (red).

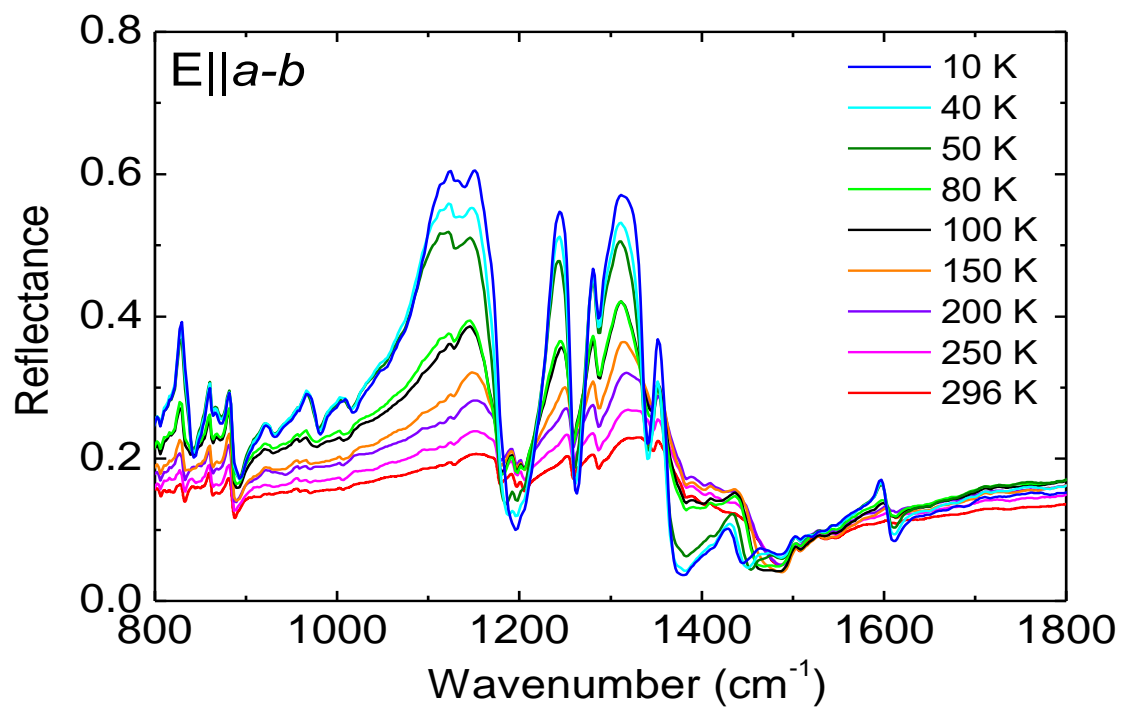


Figure S4. Temperature dependence of the reflectance spectra of (EDT-TTF-I₂)₂TCNQF for polarization $E \parallel a-b$ within frequency region 800-1800 cm⁻¹ (adopted from Ref. [5])

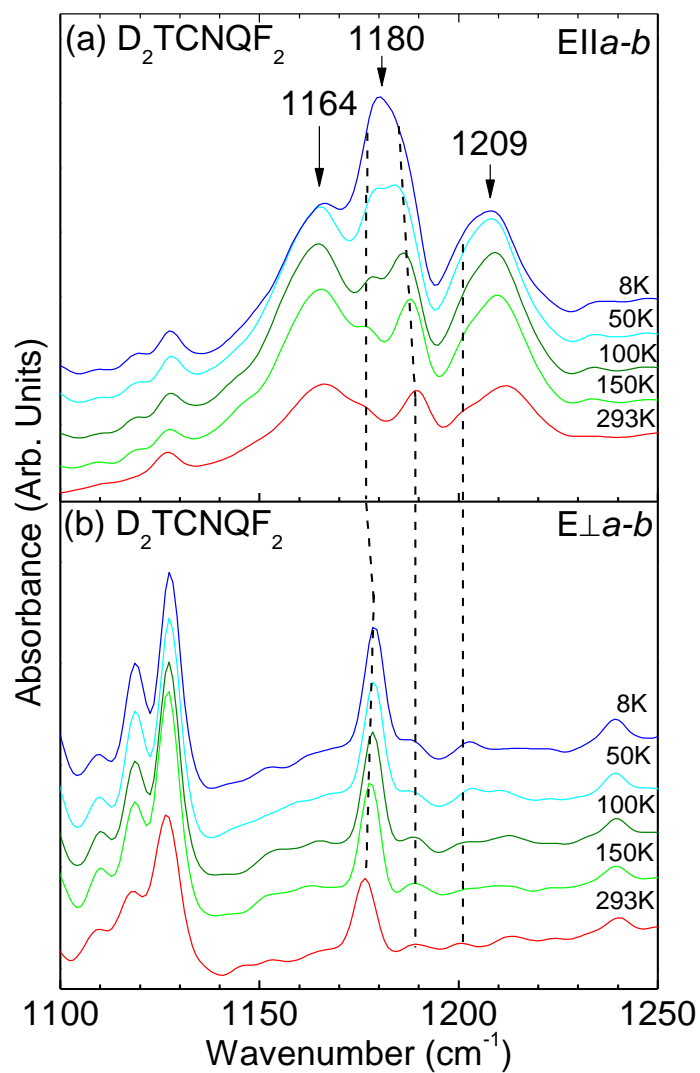


Figure S5. Temperature dependence of IR absorbance spectra of the D_2TCNQF_2 single crystal for polarizations $E||a-b$ (a) and $E\perp a-b$ (b) within frequency region 1110-1250 cm^{-1} .

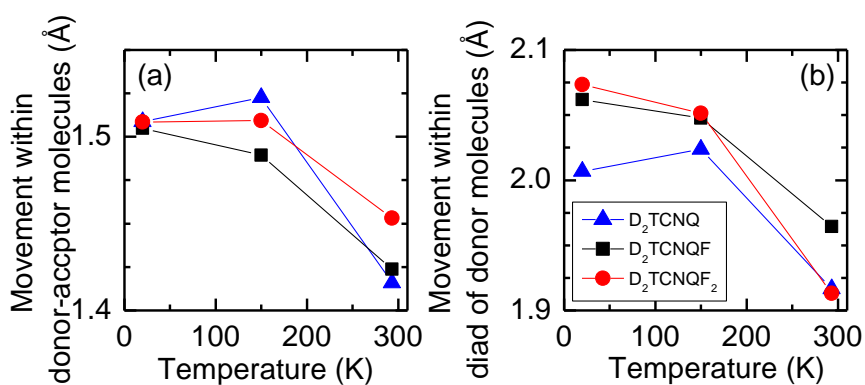


Figure S6. Temperature-induced shift of molecules within (a) donor-acceptor pair and (b) diad of donor molecules in the D_2TCNQ , D_2TCNQF , and D_2TCNQF_2 complexes.

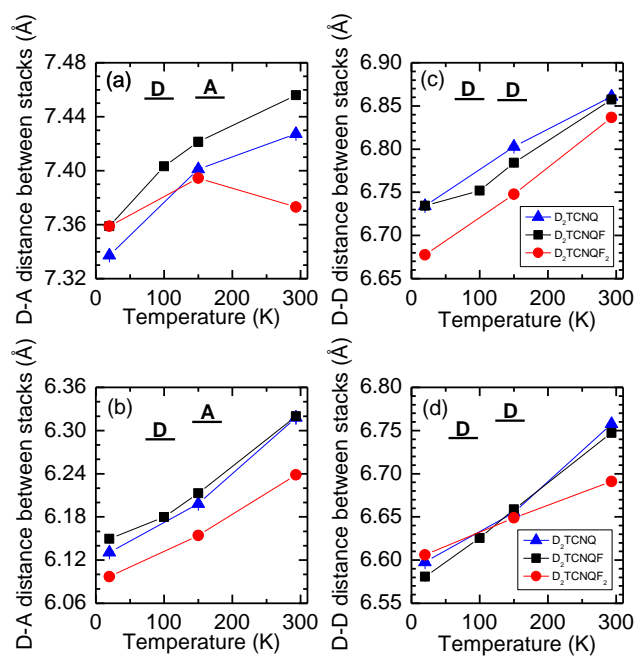


Figure S7. Distance between centroids of (a) side-by-side donor and acceptor molecules, (b) diagonal donor and acceptor molecules, (c) side-by-side donor molecules, (d) diagonal donor molecules from neighbouring stacks in the D₂TCNQ, D₂TCNQF, and D₂TCNQF₂ complexes for several temperatures (error bars are smaller than the size of the points).

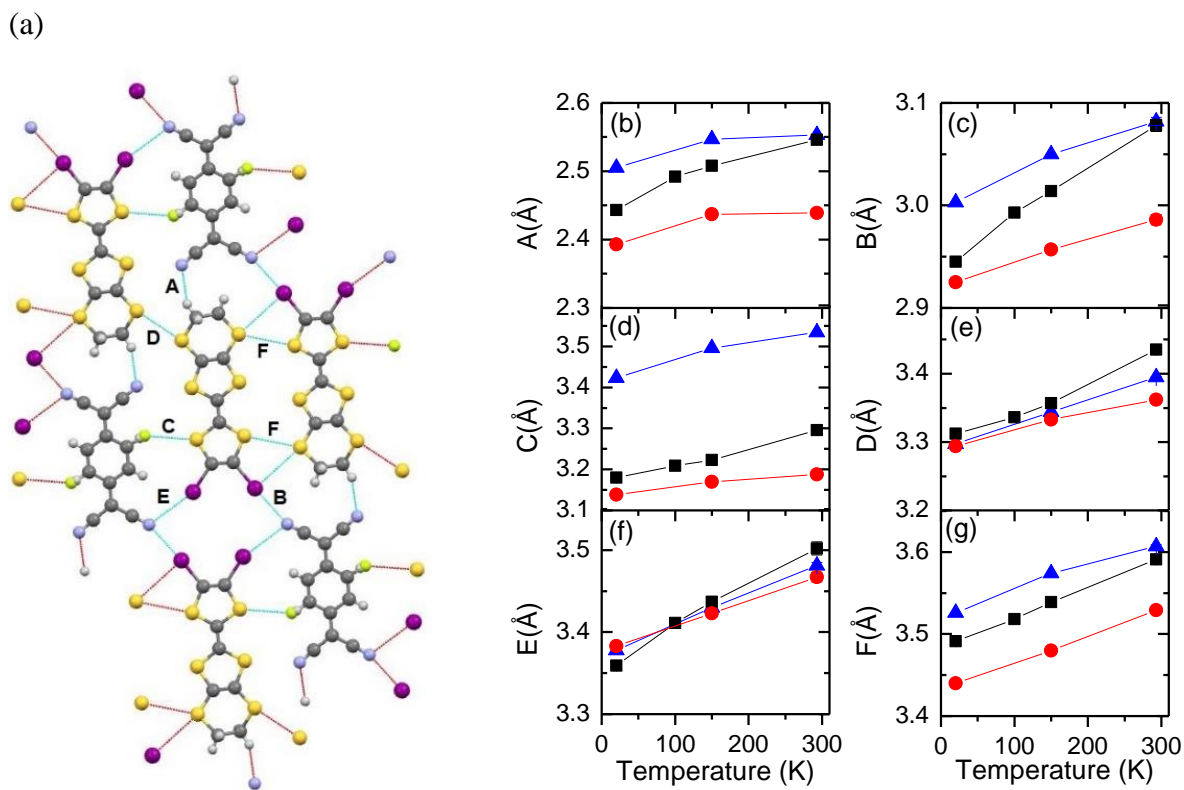


Figure S8. (a) Projection view of a layer in the isostructural series of the D_2TCNQ , D_2TCNQF , and D_2TCNQF_2 complexes; temperature dependence of short contacts between: (b) hydrogen and nitrogen atoms (D-A), (c) iodine and nitrogen atoms (D-A), (d) fluorine (or hydrogen atom in case of D_2TCNQ) and sulphur atoms (D-A), (e) sulphur atoms (D-D), (f) iodine and nitrogen atoms (D-A), (g) sulphur atoms (D-D) from neighbouring stacks (error bars are smaller than the size of the points).

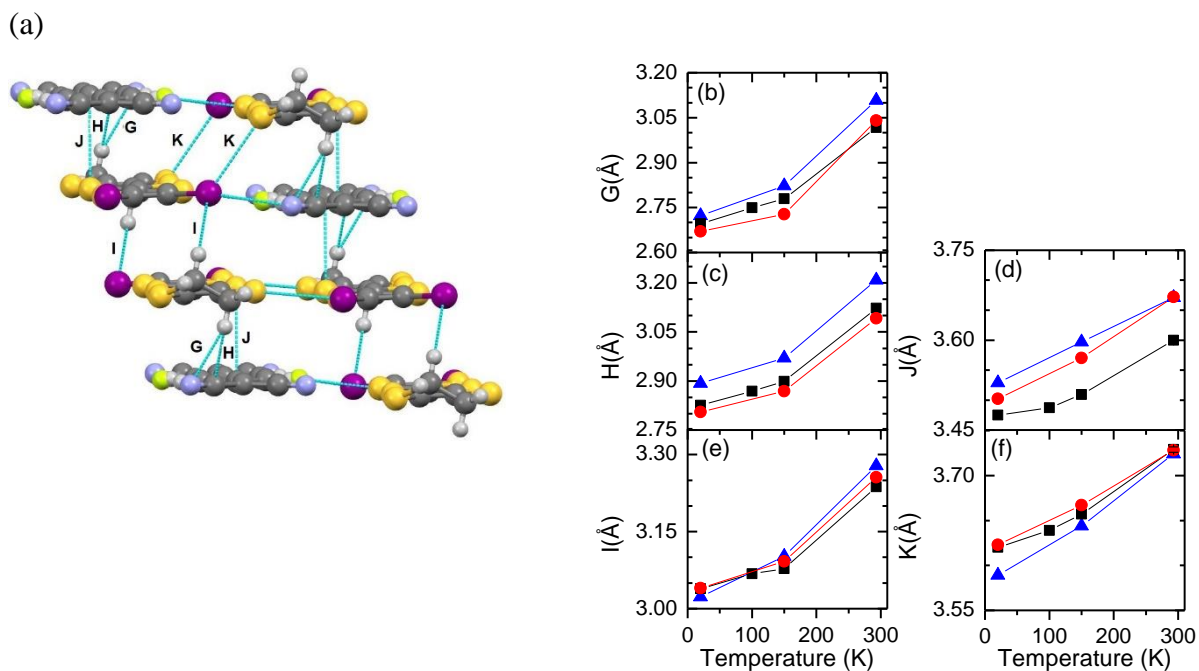


Figure S9. (a) Projection view of mixed-stacks in the isostructural series of the D_2TCNQ , D_2TCNQF , and D_2TCNQF_2 complexes along long molecular axis of donor and acceptor molecules along c -axis; temperature dependence of short contacts between: (b) hydrogen and nitrogen atoms (D-A), (c) carbon and hydrogen atoms (D-A), (d) iodine and hydrogen atoms (D-D), (e) carbon and sulphur atoms (D-A), (f) iodine and sulphur atoms (D-D) (error bars are smaller than the size of the points).

Table S1. Frequencies of normal modes of the TCNQ⁰ neutral molecule and the TCNQ⁻ anion in theoretical infrared and Raman spectra.

Frequency*				Description
IR		Raman		
TCNQ ⁰	TCNQ ⁻	TCNQ ⁰	TCNQ ⁻	
-	-	585	603	C-C-C b
-	-	611	586	def oop
-	-	699	712	Def ring
-	-	743	719	Def oop
846	825	-	-	C-H oop
-	-	938	963	C-C-C b, def ring
1098	1104	-	-	C-H b, C-C str
-	-	1165	1184	C-C str, C-H b
1188	1191			C-C str, C-H b
-	-	1193	1183	C-H b, C-C str
1333	1298	-	-	C-C str
1382	1330	-	-	C=C str, C-H b
-	-	1439	1347	C=C str
1528	1487	-	-	C=C str, C-H b
1541	1461	-	-	C=C str, C-H b
-	-	1617	1599	C=C str, C-H b
2232	2171	-	-	C≡N str
2249	2202	-	-	C≡N str

* in cm⁻¹ units

str – stretching; b – bending; def – deformation of molecule; oop – out of plane

Table S2. Frequencies of normal modes of the TCNQF⁰ neutral molecule and the TCNQF⁻ anion in theoretical infrared and Raman spectra.

Frequency*				Description
IR		Raman		
TCNQF ⁰	TCNQF ⁻	TCNQF ⁰	TCNQF ⁻	
600	611			C-C b
-	-	658	673	def ring
-	-	710	683	def oop
813	804	-	-	C-H b oop
859	858	-	-	def ring, C-F str
866	843	-	-	C-H b oop
-	-	950	967	def ring
-	-	983	1007	C-H b
1098	1108	1098	1108	C-H b, C-F str, C-C str
1162	1174	1162	1174	C-C str, C-H b, C-F str
-	-	1187	1189	C-H b, C-C str, C-F str
1207	1191	1207	1191	C-F str, C-H b, C-C str
1245	1244	1245	1244	C-H b, C-C str, C-F b
1333	1301	1333	1301	C-C str, C-H b
1372	1332	1372	1332	C=C str, C-H b
1445	1361	1445	1361	C=C str
1425	1458	1425	1458	C=C str
1527	1477	1527	1477	C-C str, C-H b
1554	1494	1554	1494	C=C str, C-H b
1625	1604	1625	1604	C=C str, C-H b
2231	2175	2231	2175	C≡N str
2233	2172	2233	2172	C≡N str
2247	2209	2247	2209	C≡N str
2251	2204	2251	2204	C≡N str

* in cm⁻¹ units

str – stretching; b – bending; def – deformation of molecule; oop – out of plane

Table S3. Frequencies of normal modes of the TCNQF₂⁰ neutral molecule and the TCNQF₂⁻ anion in theoretical infrared and Raman spectra.

Frequency*				Description
IR		Raman		
TCNQF ₂ ⁰	TCNQF ₂ ⁻	TCNQF ₂ ⁰	TCNQF ₂ ⁻	
-	-	613	606	C-C-C b
-	-	600	585	Def oop
-	-	662	677	Def ring
-	-	682	648	Def oop
694	660	-	-	Def oop
780	771	-	-	C-F str
868	853	-	-	C-H b oop
-	-	894	899	Def ring, C-F str
985	1004	-	-	C-C-C b, C-H b
1127	1138	-	-	C-C str, C-H b, C-F str
-	-	1152	1165	C-C str, C-H b
1206	1194	-	-	C-C str, C-H b, C-F str
-	-	1206	1185	C-F str
-	-	1236	1233	C-H b, C-C str
1283	1269	-	-	C-C str, C-H b
1368	1318	-	-	C-C str, C-H b
-	-	1424	1482	C-C str, C-H b
-	-	1448	1371	C=C str
1526	1443	-	-	C=C str
1568	1504	-	-	C=C str, C-F str, C-H b
-	-	1632	1609	C=C str, C-H b
2233	2176	-	-	C=N str
-	-	2234	2176	C=N str
-	-	2248	2211	C=N str
2251	2207	-	-	C=N str

* in cm⁻¹ units

str – stretching; b – bending; def – deformation of molecule; oop – out of plane

Table S4. Experimental IR and Raman frequencies of (EDT-TTF-I₂)₂TCNQ, EDT-TTF-I₂⁰ at room-temperature

Frequency (cm ⁻¹)*					Description
IR			Raman		
D ₂ TCNQ			D ₂ TCNQ		
E⊥a-b [†]	E a-b [‡]	D ^{0**}	E⊥a-b	D ^{0**}	
-	-	594	582vw	590	D: C-S str.
-	-	-	609w	-	A: C-C-C b.
-	-	649	649vw	649	D: C-S str.
-	-	-	685vw	-	A: def. ip.
-	-	696	708s	696	D: C-S, C-I str.; A: def. oop.
789m	-	767	-	-	D: C-S, C-I str.; A: C-H oop.
864w	-	882	885w	828	D: C-S str.
919vw,929vw	-	917	913vw	910	D: C-S str., C-I str.
-	-	-	953w	-	A: C-H def. oop.
1010vw,1016w	-	1005	1003vw	1005	D: C-S str.; A: C-C-C b.
1160vw	-	1125	1181w,1185w		D: H-C-H b.; A: C-C str., C-H b.
1207s	-	1173	1192vs	1174	D: H-C-H b.; A: C-H b.
-	-	-	1220vw	-	A: C-C str., C-H b.
1261vw	-	1284	1290vw	1285	D: H-C-H b., A: C-C str., C-H b.
1348s,1373	1348vw,1374vw	-	1314vw	-	A: C=C str.; C-H b.
1403vw	-	1407	1412vw	-	D: H-C-H b.
1463,1485vw	1442,1451,1463	1552	1431m,1461vw,1468vw	1552	D: C=C str.
1518s,1532s	1515vw,1533vw	-	1490w	-	A: C=C str., C-H b.

-	-	1492	1493vw	1495	D: C=C str.
-	-	1515	1515vw,1541vw	1515	D: C=C str.
-	-	-	1598s	-	A: C=C str., C-H b.
1709vw	-	-	-	-	?
-	-	-	1900vw,1923vw	-	?
1983vw	-	-	-	-	?
2115vw	-	-	-	-	?
2128w	-	-	-	-	?
2166vs	-	-	-	-	A: C≡N str.
2190w	-	-	2189vw	-	A: C≡N str.
2209w	-	-	2211s	-	A: C≡N str.
2270vw,2274vw	-	-	-	-	A: C≡N str.
2853vw,2927vw	-	-	-	-	D: A: C-H str.
3046w	-	-	-	-	D: A: C-H str.

D: donor mode; A: acceptor mode;

Approximate mode description: str., stretching; b., bending;

def., deformation vibration of the ring; oop., out of plane; ip., in plane.

* vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder;

** Ref. [Łapiński, A.; Ouahab, L.; Imakubo, T. Vib. Spectrosc. 2010, 52, 22–30];

† absorbance spectrum

‡ optical conductivity spectrum

Table S5. Experimental IR and Raman frequencies of (EDT-TTF-I₂)₂TCNQF, EDT-TTF-I₂⁰, and TCNQF⁰ at room-temperature

Frequency (cm ⁻¹) ^a							Description
IR				Raman			
D ₂ TCNQF				D ₂ TCNQF			
E a-b [†]	E a-b [‡]	D ^{0*}	TCNQF ^{0**}	E a-b	D ^{0*}	TCNQF ⁰	
-	-	594	-	-	590	599w	D: C-S str., A: def. oop.
-	-	-	-	608vw	-	605w	A: C-C-C b.
-	-	-	-	-	-	614vw	A: C-C-C b.
-	-	649	651vw	648vw	649	652vw	D: C-S str., A: def.
673vw	-	-	669vw	669s	-	671m	A: def. ip.
683vw	-	-	-	-	-	-	A: def. oop.
700m	-	696	705vw	-	696	-	D: C-S, C-I str.; A: def. ip.
721vw	-	-	-	721vw	-	-	A: def. oop.
739vw	-	-	-	-	-	737m	A: def. oop.
771w	-	767	-	770vw	-	-	D: C-S, C-I str.
805w	797vw,803vw	-	813m,817m,821m	-	-	-	A: C-H oop.
831w	829w	828	849w	-	-	-	D: C-S str.; A: C-H oop.
865,884s	860,882w	851	873m,883m,891m	884w	-	-	D: H-C-H b., A: def. ip.
914w	-	917	-	913vw	910	-	D: C-S str., C-I str.
969vw	957,967w	995	-	968w	995	964w,973vw,998vw	D: C-C str., H-C-H b; A: def. ip.
999,1011w	1003w	1005	-	1005vw	1005	-	D: C-S str.
1115,1126m	1125w	1125	1112w,1118w	-	1126	1113vw	D: H-C-H b., A: C-C str.
1177sh,1204s	1173,1192,1202w	-	1203m,1208m	1167vw,1177,1194vs	-	1163vw,1182m,1198w,1205w	A: C-C str., C-F str., C-H b.
1256,1264	1255sh	1173	-	1257s	1174	-	D: H-C-H b.
1286w	1282sh	1284	-	-	1285	1263m	D: H-C-H b., A: C-C str., C-H b.
1349w	1332,1352vs	1552	1353w	1344,1369vs,br	1552	1355m	D: C=C str. A: C=C str., C-H b.
1383m	1389sh,w	-	1384w,1390m	1392sh	-	-	A: C=C str., C-F str.
1407,1415w	1409,1436sh,vw	1407	-	-	-	-	D: C-H b., A: C=C str., C-H b.
1440,1455,1504w	1504w	1492	1446w	1457,1481sh	1495	1457s,1461vs,1473m	D: A: C=C str.; D: H-C-H b.
1534, 1543vs,br	1530w	1515	1549s,1557s	1536sh	1515	1560vw	D: C=C str.
1607m,1613sh	1605w	-	-	1608,1612s	-	1607vw	A: C=C str., C-H b.
1632vw	-	-	1617m,1631	-	-	1620s,1633w	A: C=C str., C-H b.
1665vw	-	-	-	-	-	-	A: C=C str., C-H b.
1720vw	-	-	1716	-	-	-	?
1764vw	-	-	1761vw,1778vw	-	-	-	?
-	1872,1911	-	-	-	-	-	?
-	-	-	2217m	2212sh	-	2168vw	A: C=N str.
-	-	-	-	-	-	2197vw	A: C=N str.
2207m	2178sh,2195m	-	-	2199m,2211sh	-	2223s	A: C=N str.

2181vw,2223sh	2211,2221vw	-	2223s	-	-	-	A: C≡N str.
2258	-	-	-	-	-	-	?
2667	2620	-	-	-	-	-	?
-	2774	-	-	-	-	-	?
2851m	-	-	-	-	-	-	D: C-H str.
2919m,2923m	-	-	2990	-	-	-	D: C-H str.
3041w,3051m	3048	-	3070	-	-	-	D: C-H str.
-	3695	-	-	-	-	-	?

D: donor mode; A: acceptor mode;

Approximate mode description: str., stretching; b., bending;

def., deformation vibration of the ring; oop., out of plane; ip., in plane.

* vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder;

** Ref. [Lapiński, A.; Ouahab, L.; Imakubo, T. *Vib. Spectrosc.* 2010, 52, 22–30];

*** KBr pellet

† absorbance spectrum

‡ optical conductivity spectrum

Table S6. Experimental IR and Raman frequencies of (EDT-TTF-I₂)₂TCNQF₂, EDT-TTF-I₂⁰, and TCNQF₂⁰ at room-temperature

Frequency (cm ⁻¹) ^a							Description
IR				Raman			
D ₂ TCNQF ₂		D ^{0*}	TCNQF ₂ ^{0**}	D ₂ TCNQF ₂		TCNQF ₂ ⁰	
E a-b [†]	E a-b [†]			E a-b	D ^{0*}		
-	-	-	608w,617vw	607w	-	602m	A: def. ip.
-	-	-	649vw	647w	-	630w	A: def. oop
-	-	-	669w,677vw	-	-	676w	A: def. oop
-	-	696	697vw	706s	696	-	D: C-S, C-I str.; A: def. ip
722vw,732vw	719w,733w	-	720vw	-	-	726w	A: def. oop.
770w	770vw	767	792s	-	-	-	D: C-S, C-I str.
-	-	-	814vw	-	-	810vw,821vw	A: C-F str.
832w	832m	828	843vw	-	-	878vw	D: C-S str., A: def. oop.
866vw,883m	866vw,884m	882	865vw	885w	828	896vw,903vw	D: H-C-H b., A: def. oop.
914w	926vw	917	910m	911vw	910	911vw	D: C-S str., C-I str.; A: C-C-C b.
-	965w,970w	963	-	951w	967	942vw,948vw	D: C-C str., H-C-H b.; A: C-C str.
-	-	995	985vw	-	995	987vw	A: C-C-C b, H-C-H b.
998w,1010vw	989vw,996w	1005	-	-	1005	-	D: C-S str.
-	-	-	1003vw,1014vw	-	-	995vw,1004vw	A: C-C-C b, H-C-H b.
-	-	-	1039vw	-	-	-	A: C-C-C b, H-C-H b.
1096vw	1094vw	-	1063vw,1070vw	-	-	1077vw	A: C-C-C b, H-C-H b.
1110vw,1118vw,1127w	1127w	1125	1137m	-	1126	1130vw,1136vw	D: C-H b., A: C-C str., C-H b.
1177vw	1166w,1175vw	1173	1157vw	-	1174	1161w,1173m	D: H-C-H b., A: C-C-C b, H-C-H b
-	1189w	-	1186vw	1190s	-	1184m	A: C-C str., C=C str., C-F str.
-	1203vw,1212w	-	1200s	-	-	1202vw,1206vw	A: C-C str., C-H b., C-F str.
-	-	-	1233vw	-	-	1232vw	A: C-C str., C-H b.
1264vw	1264w	1256	1250vw	-	1257	1258w,1263m	A: C-C str., C-H b.
1286w	1285vw	1284	-	1283	1285	1289vw	D: H-C-H b., A: C-C str., C-H b.
-	-	-	1309	-	-	1305vw	A: C-C str., C=C str.
1349m	1359m	-	1330,1340	-	-	1352vw	A: C-C str., C-H b.
1377w	1378m	-	1363w,1375vw	-	-	-	D: H-C-H b.
-	1395vs	-	1384w,1393s,1397sh	-	-	-	A: C-C str. C-H b.
1409vw,1415w	1410vs,1417vs	1407	-	1409sh	-	1403vw	D: H-C-H b; A: C=C str., C-H b.
-	-	-	-	1431vs	-	-	A: C=C str.
1446w,1464m	1453vs,1464vs	1461	1457vw	1461sh	1464	1447m,1451m,1460vs	D: H-C-H b.; A: C=C str., C-H b.
1483w	1484vs	1515	-	1492w	1515	-	D: C=C str.
1510vw	1508m	1492	1507vw	1512vw	1495	1505w	D: C=C str. A: C=C str., C-H b
1535m	1536m,1546m	1552	1550m	1541w	1552	1541vw	D: C=C str. A: C=C str., C-H b
-	1571vw	-	1560m,1576vs	-	-	1562vw	A: C=C str., C-H b

-	1596vw	-	-	-	-	1588vw	A: C=C str., C-H b.
1611vw	1615vw, 1620vw	-	1599w	1597s	-	1611w	A: C=C str., C-H b.
-	-	-	1628w	-	-	1628vw, 1636s, 1657w	A: C=C str., C-H b.
-	1729vw	-	-	-	-	1702vw	?
-	-	-	1795w	-	-	1781vw	?
1926vw	1890m, 1912m	-	-	-	-	-	?
-	1959w, 1974w	-	-	-	-	-	?
-	2020vw	-	1991vw	-	-	-	?
2212w	2210w, 2215m	-	2195vw, 2206w	-	-	-	A: C=N str.
-	-	-	-	2186vw	-	2179w, 2212w	A: C=N str.
-	-	-	-	2210m	-	2225m, 2233s	A: C=N str.
2190, 2231vw	2186m, 2232w	-	2219m, 2230m	-	-	-	A: C=N str.
-	2251vw	-	-	-	-	2279vw	?
-	-	-	2565vw	-	-	-	?
2670vw, 2700vw	2668s, 2699w	-	2648vw	-	-	2659vw, 2702vw	?
-	-	-	-	-	-	2837vw	?
2852s	2852vs	2905	-	-	-	-	D: C-H str.
2922vs, 2953s	2920vs, 2955s	2914	2833vw	-	2916	2860vw, 2909vw	D: C-H str.; A: C-H str.
-	-	-	2937vw	-	-	-	A: C-H str.
3041w, 3051vw	3041m, 3058m	2953	2995vw, 3015w	-	2954	-	D: C-H str.; A: C-H str.
3072vw, 3078vw	3076m	2973	3070vs	-	2972	3061vw, 3086vw	D: C-H str.; A: C-H str.
3658vw	3555m	-	3202vw	-	-	-	A: C-H str.
3752vw	3746m, 3802w, 3831m	-	-	-	-	-	?

D: donor mode; A: acceptor mode;

Approximate mode description: str., stretching; b., bending;

def., deformation vibration of the ring; oop., out of plane; ip., in plane.

* vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder;

** Ref. [Łapiński, A.; Ouahab, L.; Imakubo, T. *Vib. Spectrosc.* 2010, 52, 22–30];

*** KBr pellet

† absorbance spectrum

‡ optical conductivity spectrum