Supportive Information

Ultra low resistance at TTF-TCNQ organic interfaces

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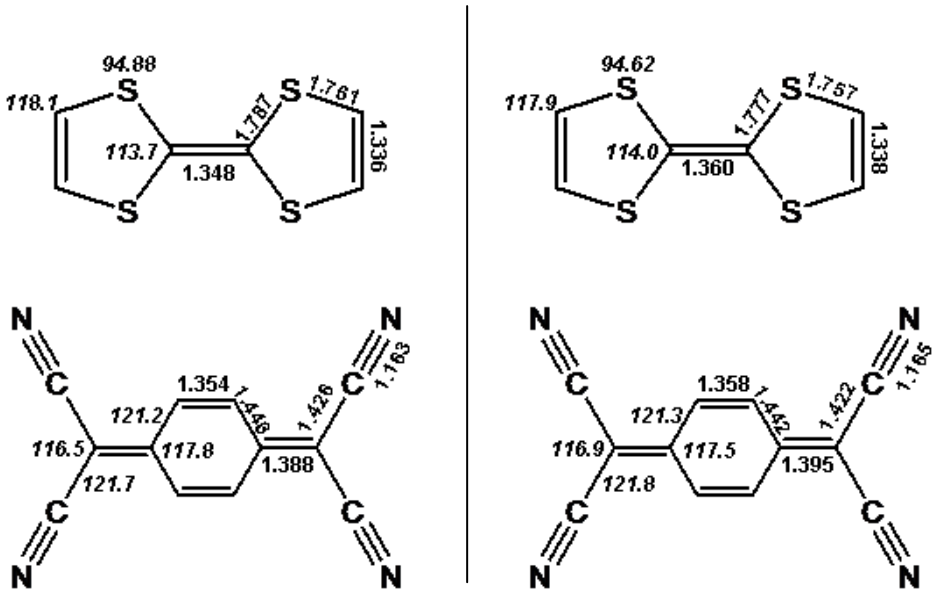
Figure S1 The geometry parameters of TTF and TCNQ. CT refers to the molecules in the charge-transfer complex. NE stays for the molecules without charge-transfer. Bond lengths are in Å, and bond angles (in italics) are in degree.

NE

CT



2，Computational methods of electronic coupling

$$V = \frac{J_{RP} - S_{RP}(H_{RR} + H_{PP})/2}{1 - S_{RP}^2}$$

Assuming h_{ks} is the system Kohn-Sham Hamiltonian which consists of two monomers, then,

for *P*-type TTF,

$$J_{RP} = \left\langle \varphi_{HOMO}^{TTF_{C1}} \middle| h_{ks} \middle| \varphi_{HOMO}^{TTF_{C2}} \right\rangle$$

$$S_{RP} = \left\langle \varphi_{HOMO}^{TTF_{C1}} \middle| \varphi_{HOMO}^{TTF_{C2}} \right\rangle$$

$$H_{RR} = \left\langle \varphi_{HOMO}^{TTF_{C1}} \middle| h_{ks} \middle| \varphi_{HOMO}^{TTF_{C1}} \right\rangle$$

$$H_{PP} = \left\langle \varphi_{HOMO}^{TTF_{C2}} \middle| h_{ks} \middle| \varphi_{HOMO}^{TTF_{C2}} \right\rangle$$

for *n*-type TCNQ,

$$J_{RP} = \left\langle \varphi_{LUMO}^{TCNQ_{C1}} \middle| h_{ks} \middle| \varphi_{LUMO}^{TCNQ_{C2}} \right\rangle$$

$$S_{RP} = \left\langle \varphi_{LUMO}^{TCNQ_{C1}} \middle| \varphi_{LUMO}^{TCNQ_{C2}} \right\rangle$$

$$H_{RR} = \left\langle \varphi_{LUMO}^{TCNQ_{C1}} \middle| h_{ks} \middle| \varphi_{LUMO}^{TCNQ_{C1}} \right\rangle$$

$$H_{PP} = \left\langle \varphi_{LUMO}^{TCNQ_{C2}} \middle| h_{ks} \middle| \varphi_{LUMO}^{TCNQ_{C2}} \right\rangle$$

The HOMO or LUMO of TFF and TCNQ used in these equations are orthogonalized by performing Löwdin's symmetric transformation.

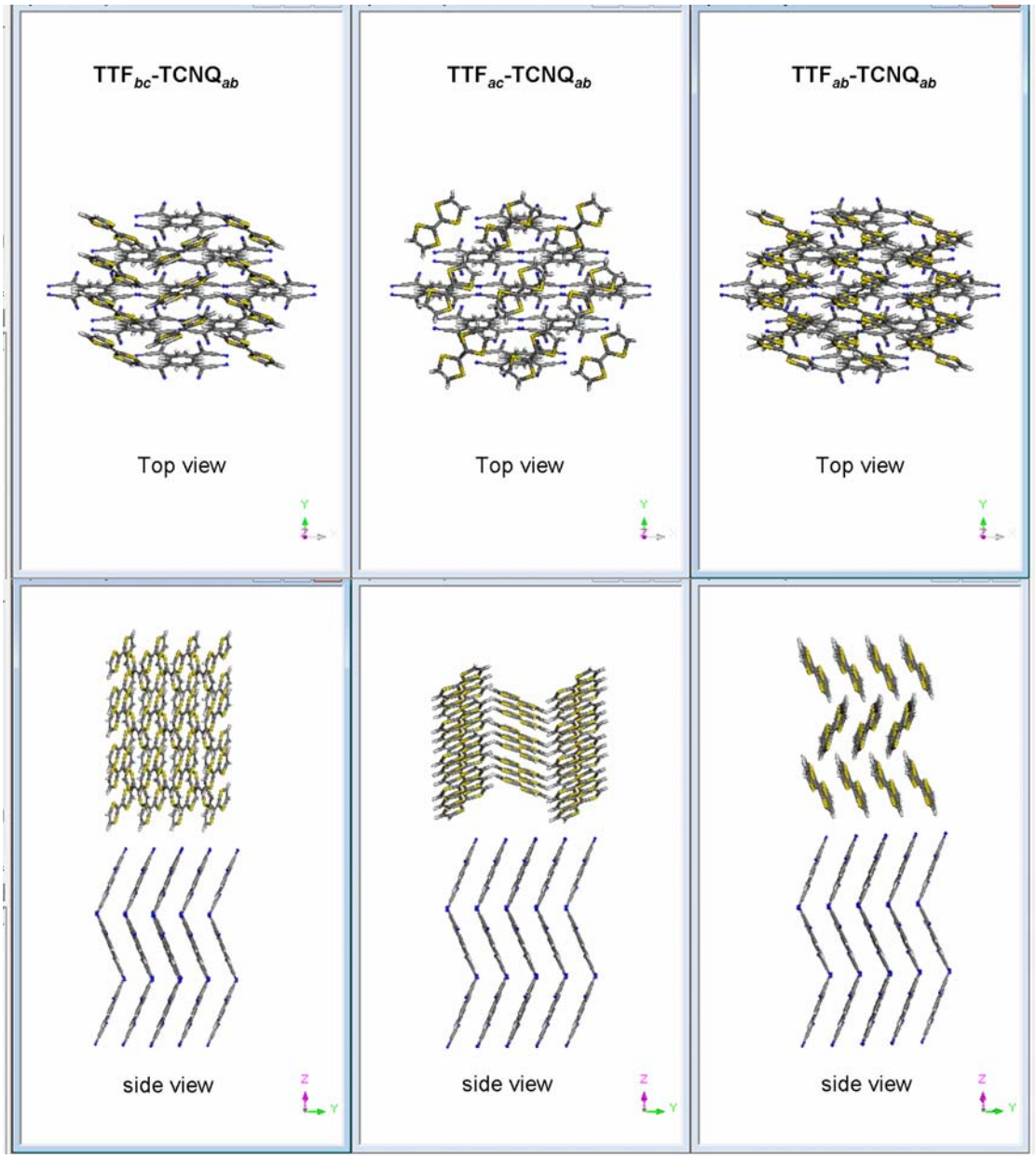
Table S1. Calculation details of electronic coupling elements including spatial overlap (S_{RP}), charge transfer integral (J_{RP}), and site energies (H_{RR}, H_{PP}). The V of Pentacene (PENT) and Rubrene (RUBR) are calculated as reference and compared with the previous work[a,b].

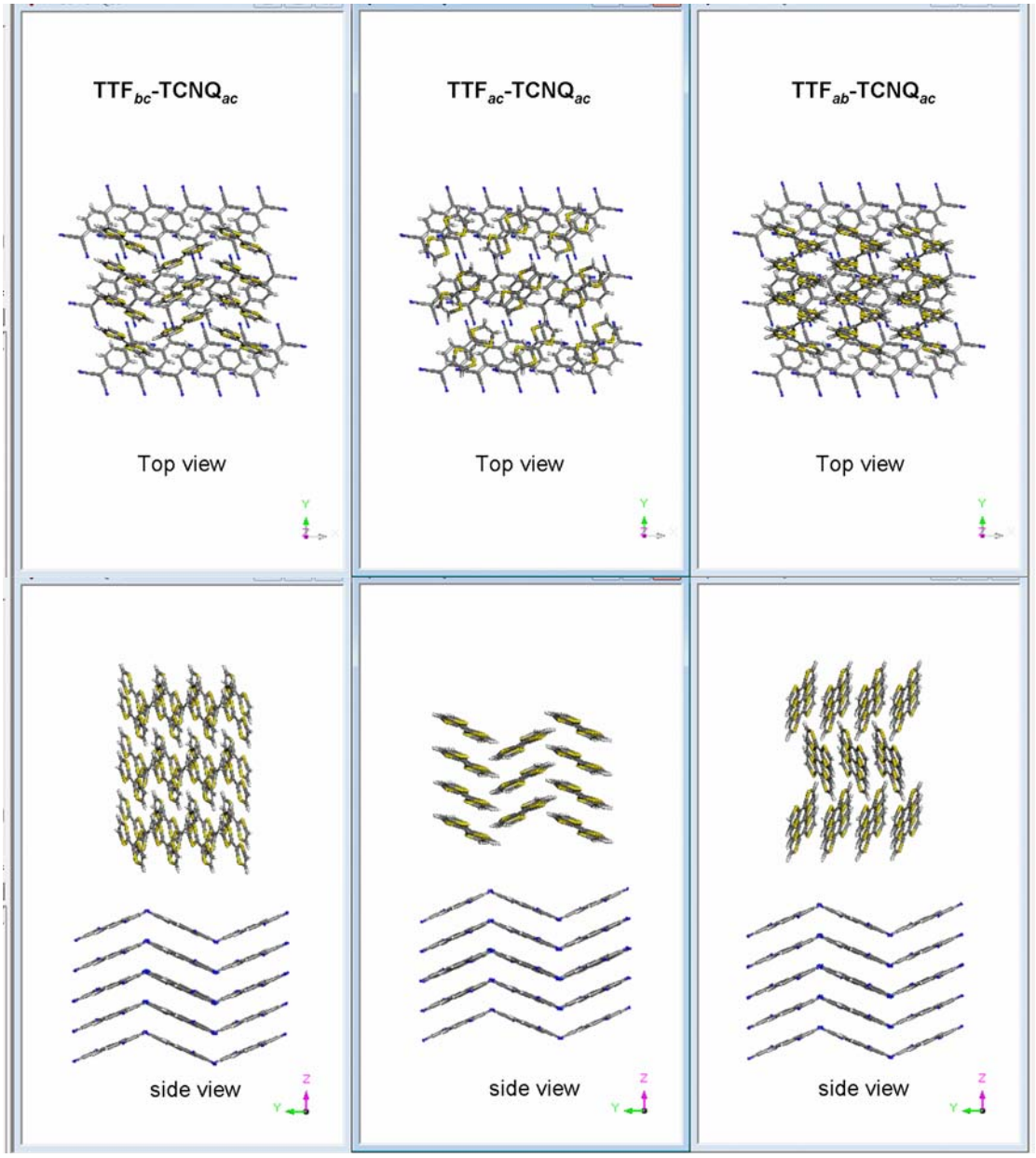
dimer	J_{RP} (Hartree)	S_{RP} (Hartree)	H_{RR} (Hartree)	H_{PP} (Hartree)	$\|V\|$ (eV)
PENT_T1	0.006148971	-0.01895235	-0.14930137	-0.17013888	0.084982407
					0.085[a]
					0.0934[b]
PENT_T2	-0.00333378	0.009910871	-0.16989312	-0.1504131	0.047530247
					0.051[a]
					0.0621[b]
PENT_P	0.002209107	-0.00616696	-0.16465155	-0.16465841	0.032483333
					0.037[a]
					0.0357[b]
PENT_L	0.00012707	-0.00046319	-0.16511826	-0.16512224	0.00013766
					0[a]
					0.00015[b]
RUBR_T1	-0.00129258	0.004178909	-0.15926568	-0.15969048	0.01903513
					0.015[a]
RUBR_T2	-0.00129241	0.004178930	-0.15926713	-0.15968359	0.01903417
					0.015[a]
RUBR_P	0.006339604	-0.019348006	-0.15945768	-0.15945258	0.088592390
					0.083[a]
RUBR_L	0.000010137	0.0000323046	-0.16132613	-0.16132511	-0.00013404
					0[a]
TTF_T1	-1.546E-05	-1.8247E-05	-0.14835916	-0.1483481	0.000494342
TTF_T2	0.001054494	-0.00227273	-0.14761619	-0.14760314	0.019565736
TTF_T3	0.000376946	-0.00141602	-0.14470652	-0.14469519	0.004681662
TTF_P	0.008391899	-0.0294397	-0.14002637	-0.14002572	0.116282722
TTF_L1	0.00029928	0.0009518	-0.14602174	-0.15123185	0.004294469
TTF_L2	0.000996628	-0.00261408	-0.15025877	-0.14280825	0.016696562
TTF_L3	-2.0445E-06	7.56455E-06	-0.14587479	-0.14592421	2.56018E-05
TCNQ_T1	9.29E-04	-0.00251941	-0.20407437	-0.20407465	0.011299177
TCNQ_T2	0.000876645	-0.00196296	-0.20751495	-0.20750624	0.012770737
TCNQ_T3	-8.171E-05	0.000285484	-0.20642388	-0.20642285	0.000619858
TCNQ_P	0.003517281	-0.00850511	-0.2076222	-0.20761299	0.047663783
TCNQ_L1	-1.0059E-05	3.17466E-05	-0.20551763	-0.20462494	9.65743E-05

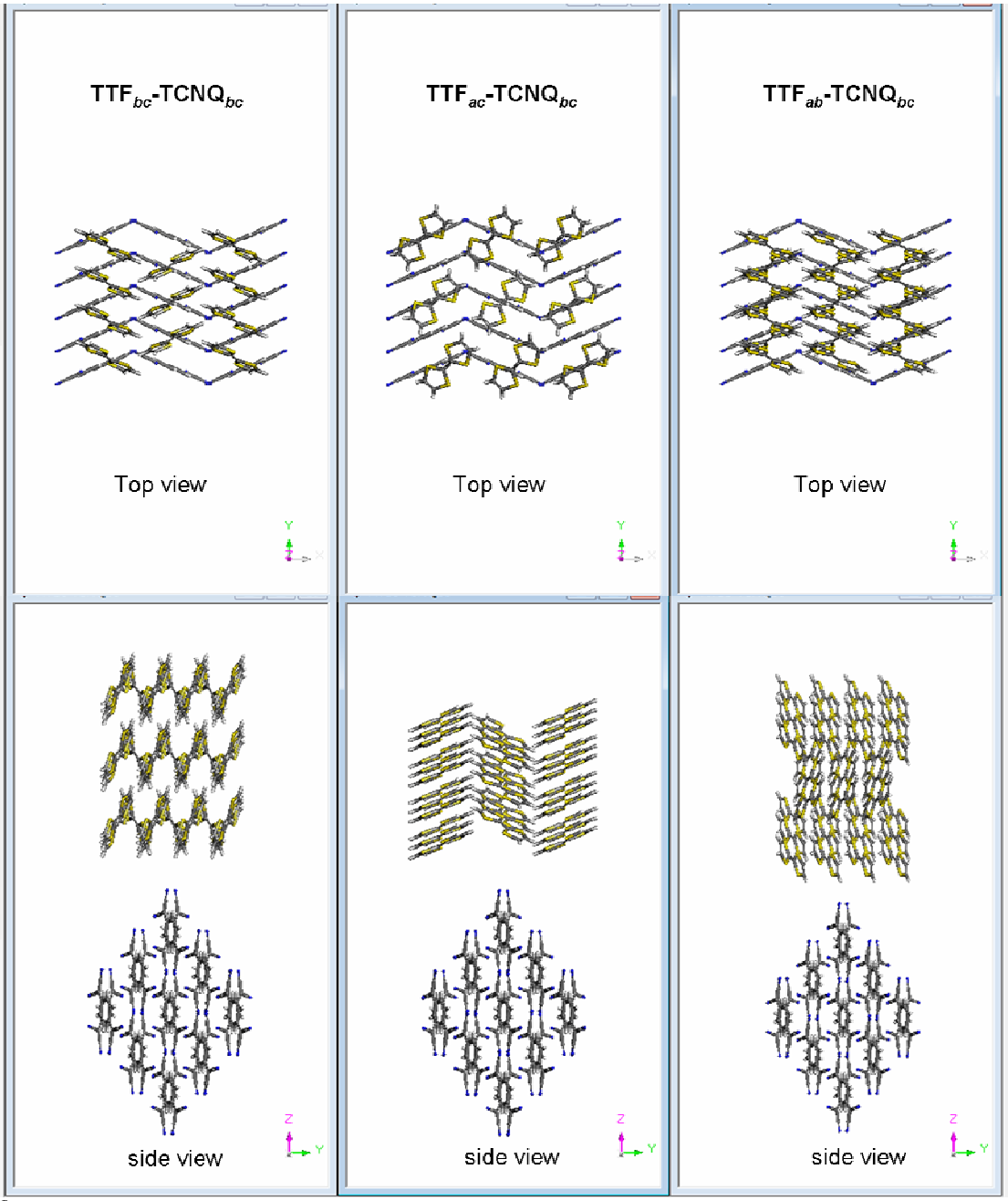
TCNQ_L2	0.000628717	-0.00168697	-0.20552611	-0.205532	0.007673586
TCNQ_L3	-0.00011615	0.000366895	-2.01E-01	-0.20149282	0.001148979

[a] Coropceanu, V.; Cornil J.; da Silva Filho, D. A.; Olivier Y.; Silbey R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926-952.
[b] Li, L. Q.; Tang, Q. X.; Li, H. X.; Yang, X. D.; Hu, W. P.; Song, Y. B.; Shuai, Z. G.; Xu, W.; Liu, Y. Q.; Zhu, D. B. *Adv. Mater.* **2007**, *19*, 2613-2617.

Figure S2, The TTF-TCNQ interface configurations with the TTF crystal *a-b, a-c or b-c* plane on the TCNQ crystal *a-b, a-c or b-c* plane (intermolecular distances at the interface > 3.5 Å considering the interface fabrication by the lamination technique[a]).




TTF$_{bc}$-TCNQ$_{ac}$
TTF$_{ac}$-TCNQ$_{ac}$
TTF$_{ab}$-TCNQ$_{ac}$
Top view
Top view
Top view
side view
side view
side view



[a] H. Alves, A. S. Molinari, H. X. Xie, A. F. Morpurgo, *Nature Materials* **2008**, *7*, 574.

Table S3，Calculation details of reorganization energy, adiabatic ionization potential (IP) and electron affinities (EA) where E_0 and $E_{+/-}$ represent the energies of the neutral and cation/anion species in their lowest energy geometries, respectively; E_0* and $E_{+/-}$* are the energies of the neutral and cation/anion states with the geometries of the cation/anion and neutral species, respectively.

$$\lambda = \lambda_0 + \lambda_{+/-} = (E_0^* - E_0) + (E_{+/-}^* - E_{+/-})$$
$$IP / EA = E_{+/-}^* - E_0$$

	λ (eV)	*IP*/*EA* (eV)	HOMO (eV)	LUMO (eV)	ΔE(eV)
TCNQ	0.2640	3.44 (3.3±0.3)[a]	-7.57	-5.01	2.56
TTF	0.2896	6.95 (6.83)[b]	-4.68	-1.03	3.65

	E_0 (Hartree)	E_0* (Hartree)	E_+ (Hartree)	E_+* (Hartree)	IP (eV)	λ (eV)
TTF	-1823.89257	-1823.88716	-1823.66156	-1823.65633	6.4283	0.2896
PENT	-846.98821	-846.98649	-846.76312	-846.76125	6.1758	0.0976
RUBR	-1617.69581	-1617.69301	-1617.47425	-1617.47148	6.1032	0.1521
	E_0 (Hartree)	E_0* (Hartree)	E_- (Hartree)	E_-* (Hartree)	EA (eV)	λ (eV)
TCNQ	-678.74325	-678.73853	-678.87479	-678.86981	3.443749	0.264

[a] C. Jin, R. E. Haufler, R. L. Hettich, C. M. Barshick, R. N. Compton, A. A. Puretzky, A. V. Demyanenko, A. A. Tuinman, *Science* **1995**, *267*, 440.
[b] E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, R. N. Compton, *J. Am. Chem. Soc.* **1975**, *97*, 2921.

Table S4. Crystal structural data of TTF, TCNQ

	TTF	TCNQ
System	Monoclinic	Monoclinic
Space group	P21/C	C2/C
a/Å	7.352	8.906
b/Å	4.0181	7.06
c/Å	13.901	16.395
α/deg	90	90
β/deg	101.426	98.53
γ/deg	90	90
D/gcm^{-3}	1.686	1.330
Volume/Å^3	402.512	1019.455
Reference	1	2

1. Cooper, W. F.; Kenny, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coppens, P. *J. Chem. Soc. D* **1971**, *16* 889-890
2. Long, R. E.; Sparks, R. A.; Truebloo.K.N. *Acta Crystallogr.* **1965**, *18*, 932-939.

Table S5. The evaluation of the electron and hole density (C, in e·cm-2) at the interface. N is the molecule amount per plane of TTF and TCNQ primitive cell; S is the area of the crystal plane (in Å2); Q (in e) is the calculated charge transfer per molecule.

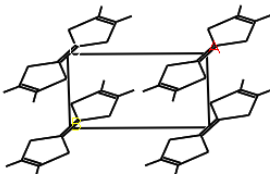
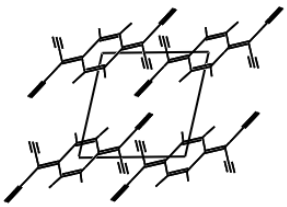
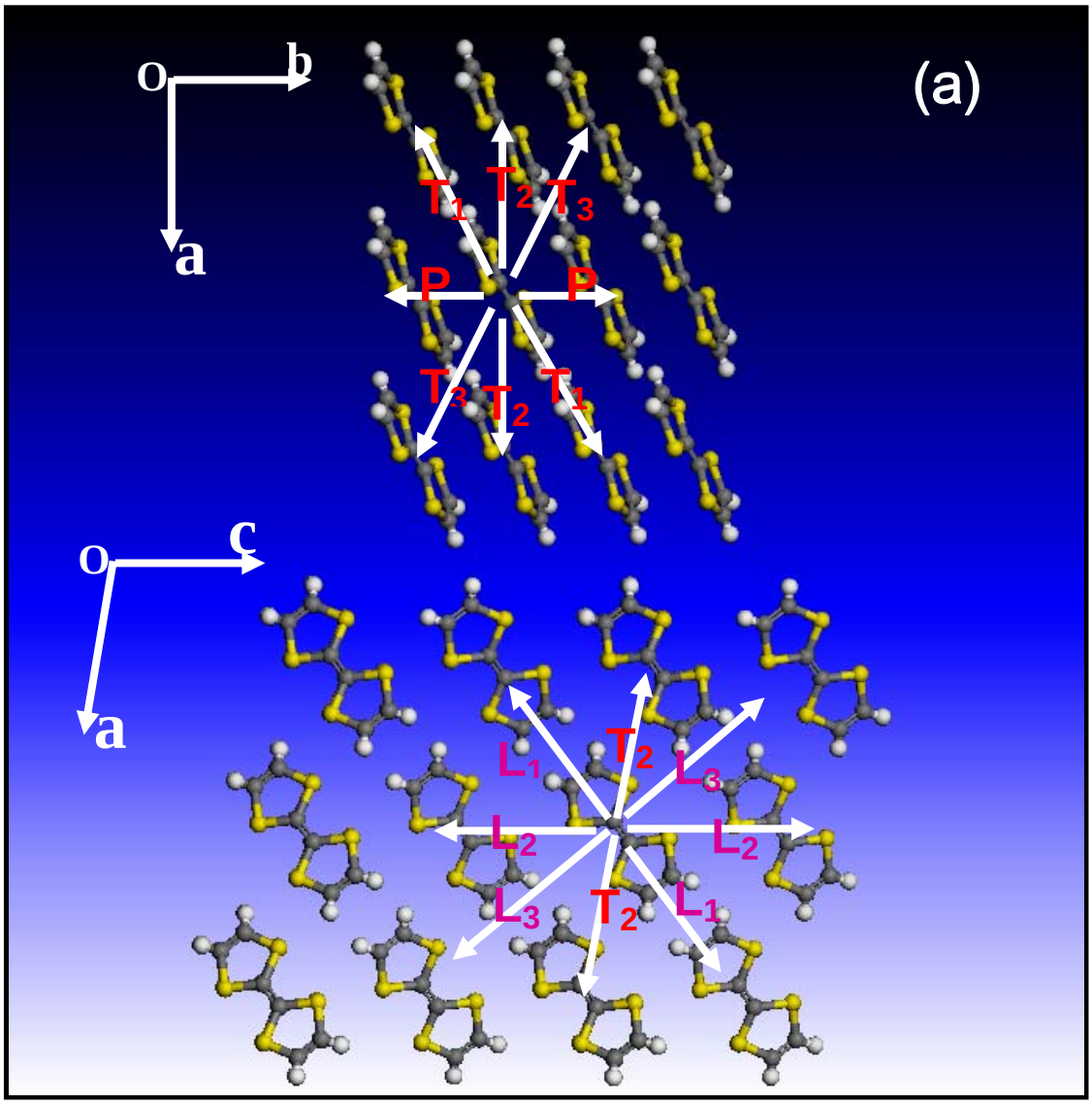
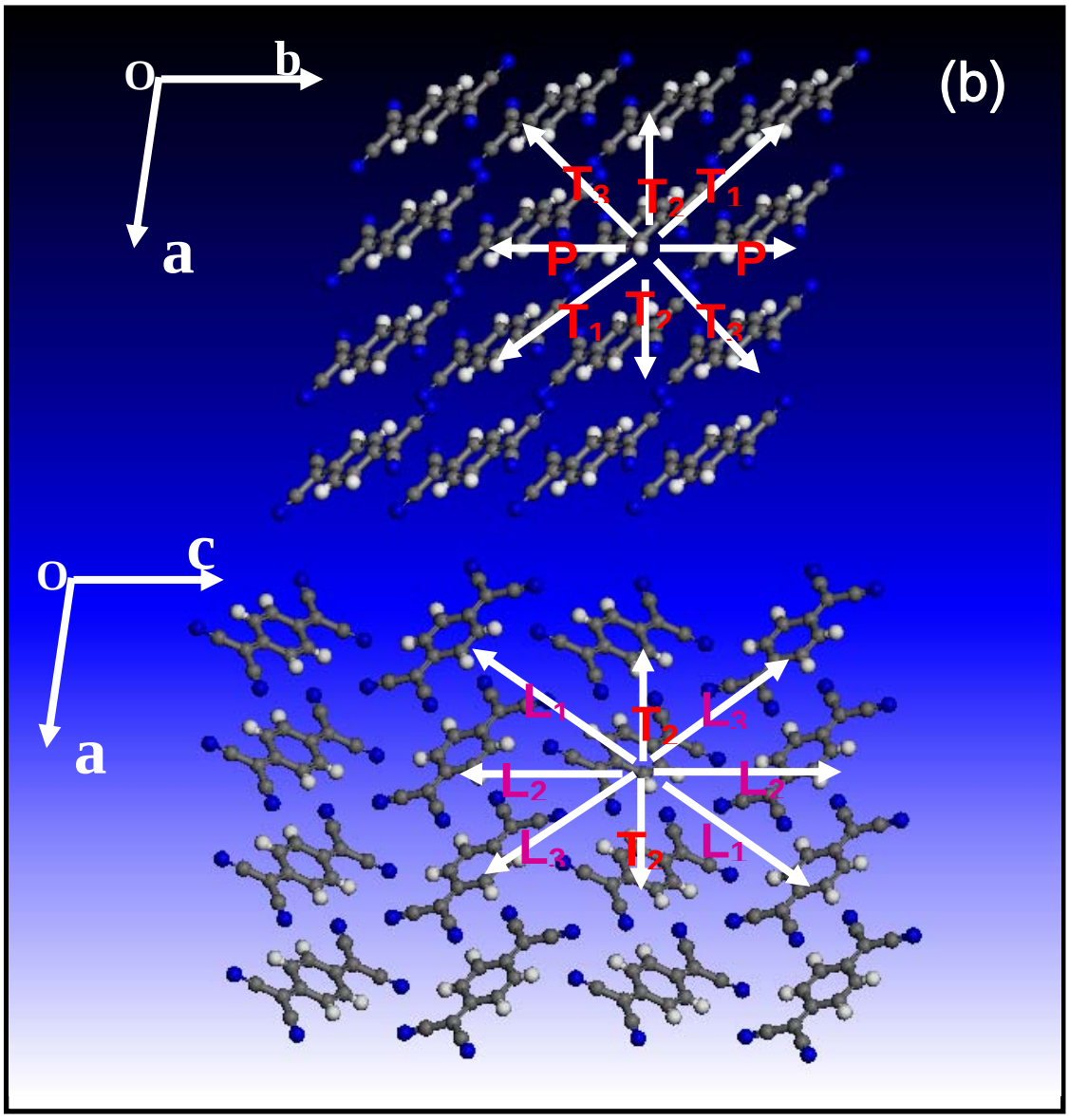
Unit *a*-*b* plane	N	S	Q	C
	1	29.54	0.2498-0.4109	(0.84-1.39)×10^{14}
	1	31.44		(0.79-1.31)×10^{14}

Figure S3，Illustration of Dimer types in TTF (a) and TCNQ (b) crystal

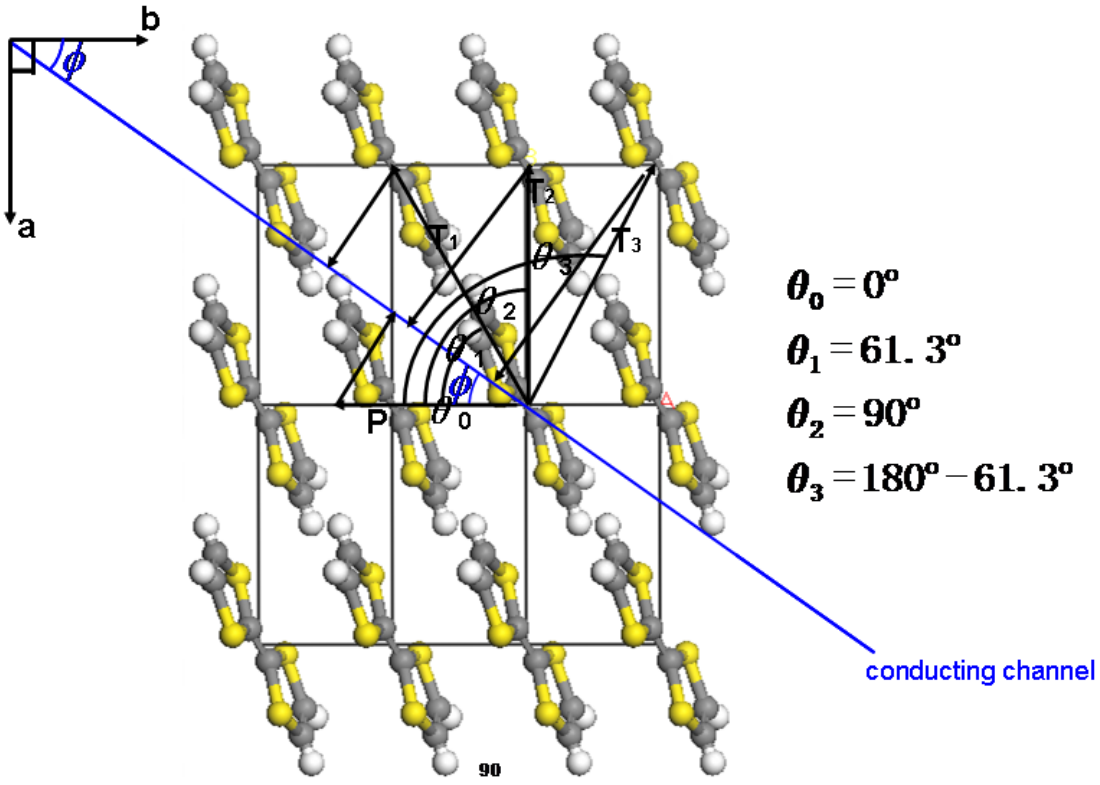


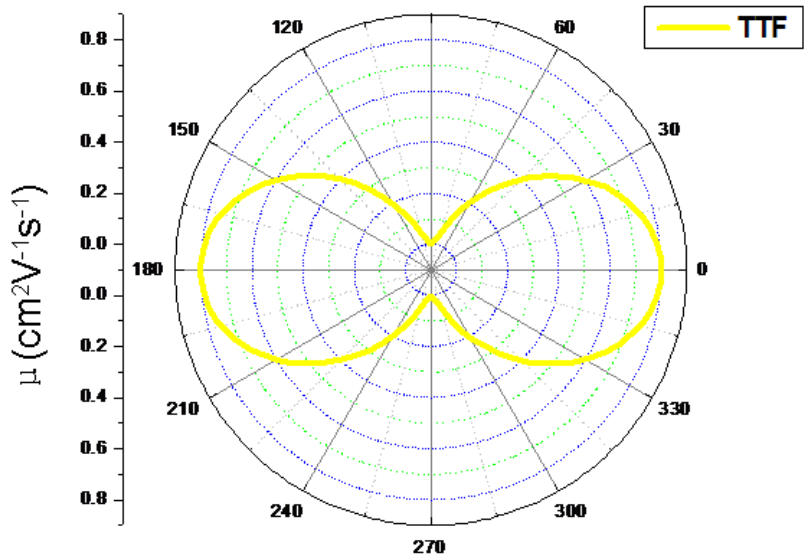
Crystal cell of TTF crystal



Primitive cell of TCNQ crystal

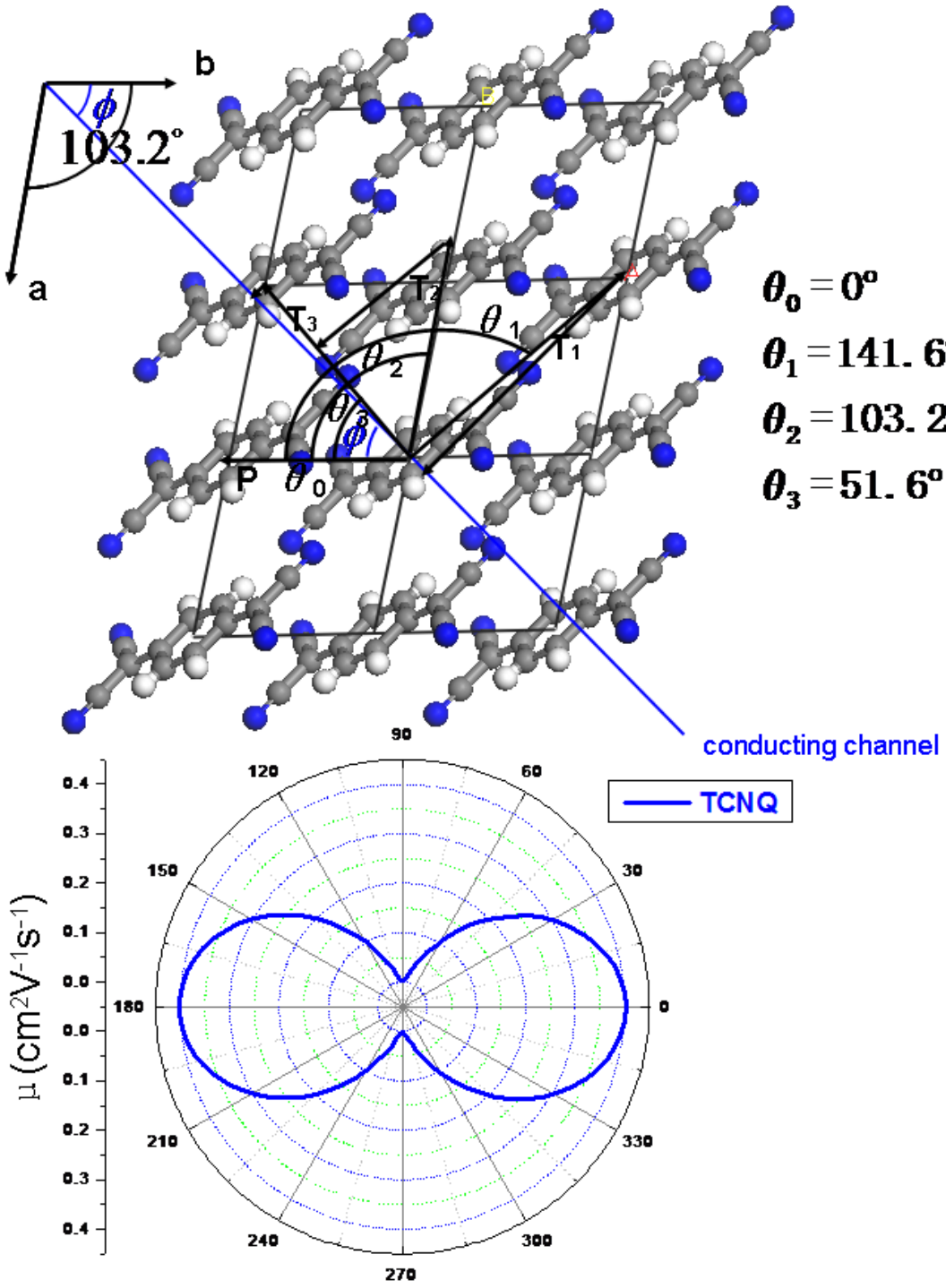
Figure S4，Illustration of projecting different hopping paths to a transistor channel in the *a*-*b* plane of TTF single crystals; (θ_0, θ_1, θ_2 and θ_3 are the angles of P, T1, T2, and T3 dimers relative to the reference crystallographic axis *b*; Φ is the angle of a conduction channel relative to the reference axis *b*.





$$\mu_\phi = 0.79\cos^2\phi + 1.13\times10^{-9}\cos^2(61.3°-\phi) + 0.95\times10^{-5}\cos^2(61.3°+\phi) + 0.24\times10^{-2}\cos^2(90°-\phi)$$

Figure S5 Illustration of projecting different hopping paths to a transistor channel in the *a*-*b* plane of TCNQ crystal primitive cell; (θ_0, θ_1, θ_2 and θ_3 are the angles of P, T1, T2, and T3 dimers relative to the reference crystallographic axis *b*; Φ is the angle of a conduction channel relative to the reference axis *b*.



$$\mu_{\phi} = 0.36\cos^2\phi + 0.21\times10^{-2}\cos^2(141.6°-\phi) + 1.63\times10^{-3}\cos^2(103.2°-\phi) + 1.32\times10^{-8}\cos^2(51.6°-\phi)$$

Supplementary Material (ESI) for Chemical Communications