

Electronic Supplementary Information:

Theoretical Study on the Charge Transport in Single Crystals of TCNQ, F₂-TCNQ and F₄-TCNQ

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S1. Selection of functional and basis set

To test the reliability of the calculated results, a series of functionals including B3LYP, B3PW91, M06-2X, ω B97XD and PBE1PBE with same basis set of 6-31+G(d,p) were employed to calculate the geometrical and electronic structures of F₂-TCNQ. The optimized geometries of F₂-TCNQ obtained from these functionals were compared with the configuration in crystal. As shown in Fig. S1, the discrepancies mainly about the bond lengths obtained from different functionals are small. The HOMO/LUMO energies, energy gaps, as well as electron reorganization energies for F₂-TCNQ at different levels are listed in Table S1. The calculated results indicate that the frontier orbital distributions obtained from these five functionals show little difference. But it is found that M06-2X and ω B97XD tend to underestimate the energy level of HOMO and overestimate the energy level of LUMO and energy gap; and the reorganization energies evaluated by these methods are much larger than other methods. While the results obtained by B3PW91, B3LYP, and PBE1PBE methods are close to each other. Unfortunately, there is no experimental LUMO values for compounds F_n-TCNQ (n = 0, 2, 4) for reference. But B3LYP has been proven suitable to describe the geometric relaxation of charge transfer process for various organic systems so far. So B3LYP functional was selected out for geometry optimizations and frequency calculations in this study. Furthermore, in order to investigate the influence of basis set, different basis 6-31G(d,p), 6-31+G(d,p), and 6-311+G(d,p) using B3LYP functional were also employed to optimize the molecular geometries of F₂-TCNQ. As shown in Fig. 1, the equilibrium geometries of F₂-TCNQ

obtained at B3LYP/6-311+G(d,p) are closest to the configuration in crystal. The HOMO/LUMO energies and energy gaps of F₂-TCNQ at different levels are listed in Table S2. It can be seen that the basis sets without diffusion functions overestimate the energy level of frontier orbital, but the effect of the diffusion functions on reorganization energy is negligible. So the B3LYP/6-311+G(d,p) was employed to characterize the electronic properties of the complexes in this work.

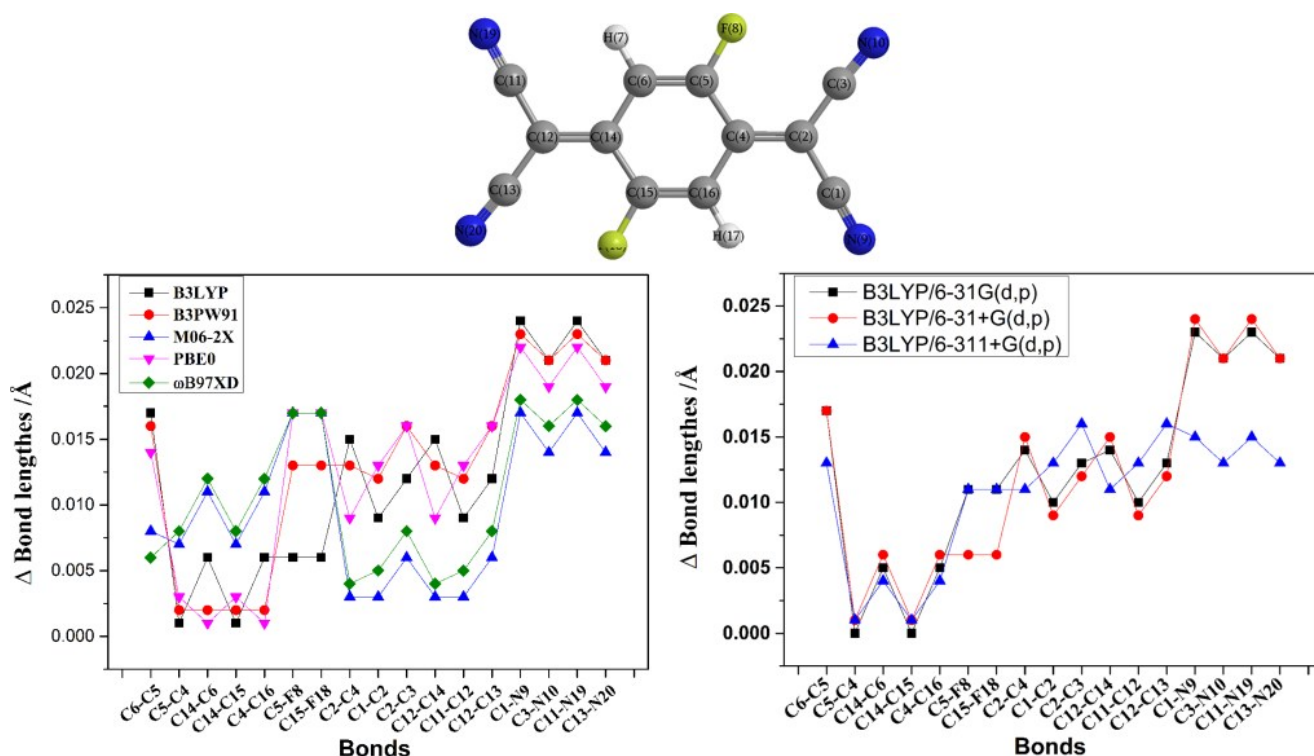


Fig. S1 the optimized bond lengths of F₂-TCNQ compared with to the configuration in crystal employing different functionals M06-2X, ωB97XD, B3PW91, B3LYP, and PBE1PBE with the same 6-31+G(d,p) basis set (left) and B3LYP with different basis sets (right). The atom indices are labeled on the molecular structures.

Table S1. Calculated HOMO/LUMO energies ($E_{\text{HOMO}}/E_{\text{LUMO}}$, in eV), energy gaps (E_g , in eV), and electron reorganization energies (λ_e , in meV) for F₂-TCNQ by different functional coupled with the same basis set 6-31+G(d,p).

F ₂ -TCNQ	M06-2X	ωB97XD	B3PW91	B3LYP	PBE1PBE
λ_e	383	405	263	267	282
HOMO	-8.97	-9.55	-7.87	-7.84	-8.01
LUMO	-4.55	-3.79	-5.42	-5.38	-5.27
E_g	4.42	5.76	2.45	2.46	2.74

Table S2. Calculated HOMO/LUMO energies ($E_{\text{HOMO}}/E_{\text{LUMO}}$, in eV), energy gaps (E_g , in eV), and electron reorganization energies (λ_e , in meV) for F₂-TCNQ by B3LYP with different basis sets.

F ₂ -TCNQ	B3LYP/6-31G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-311+G(d,p)
λ_e	262.9	267.2	278.5
HOMO	-7.49	-7.84	-7.91
LUMO	-5.03	-5.38	-5.41
E_g	2.46	2.46	2.50

Table S3. Calculated LUMO energies, adiabatic electron affinities [EA(a)] and electron reorganization energy (λ_e) at B3LYP/6-311+G(d,p) level for TCNQ, F₂-TCNQ and F₄-TCNQ compounds. (in eV)

Compounds	TCNQ	F ₂ -TCNQ	F ₄ -TCNQ
LUMO	-5.15	-5.41	-5.65
EA(a)	3.75	4.03	4.28
λ_e (NM)	0.268	0.279	0.270
λ_e (AP)	0.266	0.277	0.272

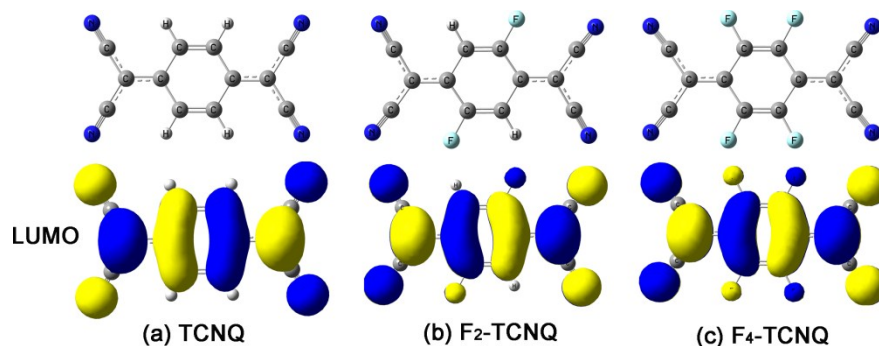


Figure S2. The optimized molecular structures and distribution of LUMO orbitals for TCNQ, F₂-TCNQ and F₄-TCNQ molecules at B3LYP/6-311+G(d,p) level.

Table S4. Lattice constants of bulk single crystalline TCNQ, F₂-TCNQ and F₄-TCNQ. (a: the ref.14)

	TCNQ ^a	F ₂ -TCNQ ^a	F ₄ -TCNQ ^a
a (Å)	8.883	10.196	9.246
b (Å)	6.594	5.923	8.096
c (Å)	16.395	8.836	14.612
α (deg)	90.000	90.000	90.000
β (deg)	98.351	106.829	90.000
γ (deg)	90.000	90.000	90.000
Space groups	C2/c	C2/m	Pbca
Temperature (K)	180	180	180

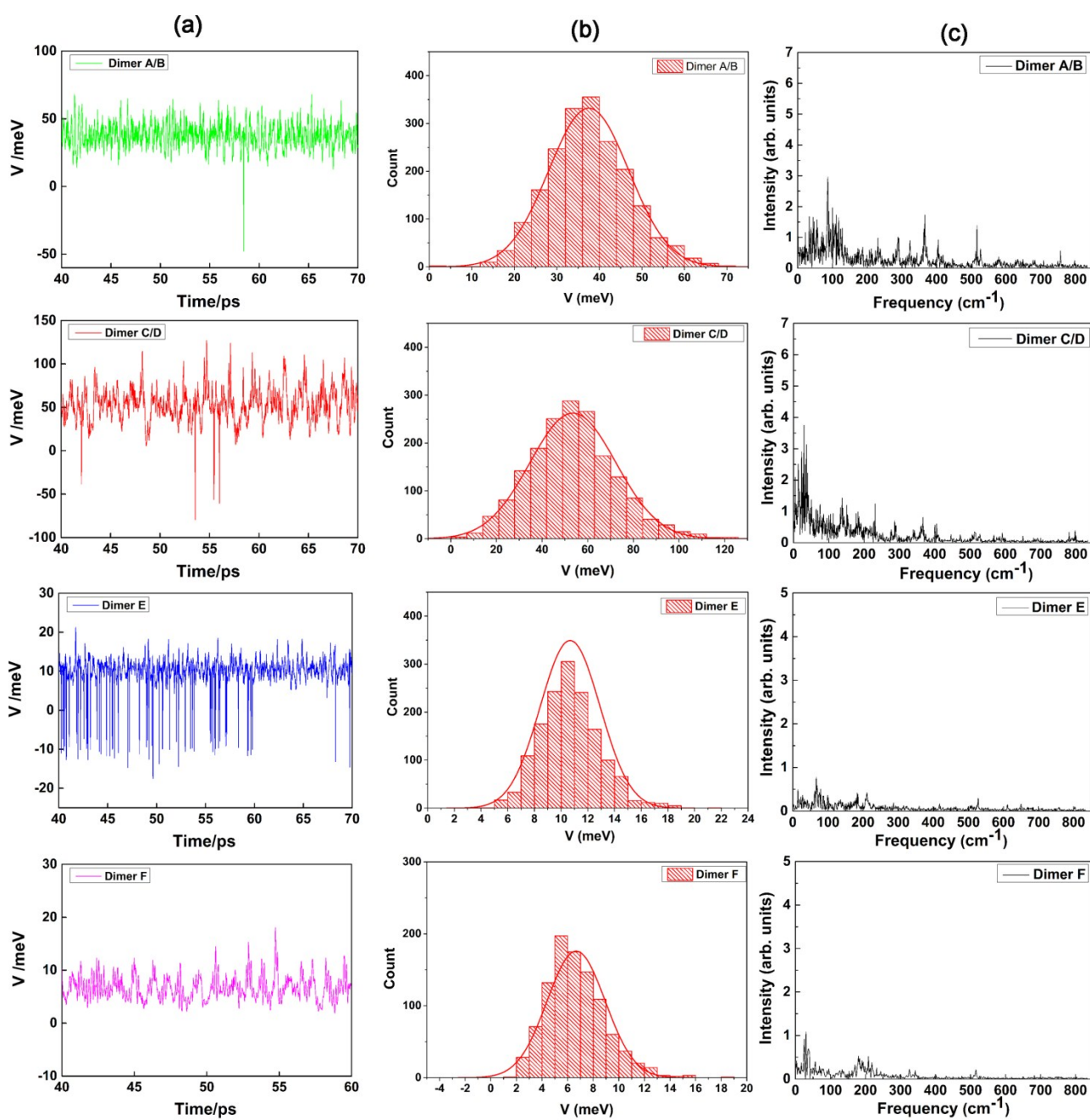


Figure S3. (a) Evolution of transfer integrals with sampling time at 300K, (b) Gaussian fitting of the transfer integrals, and (c) the contributions of vibration modes to the transfer integral fluctuation for all the transport pathways in F_2 -TCNQ crystal.

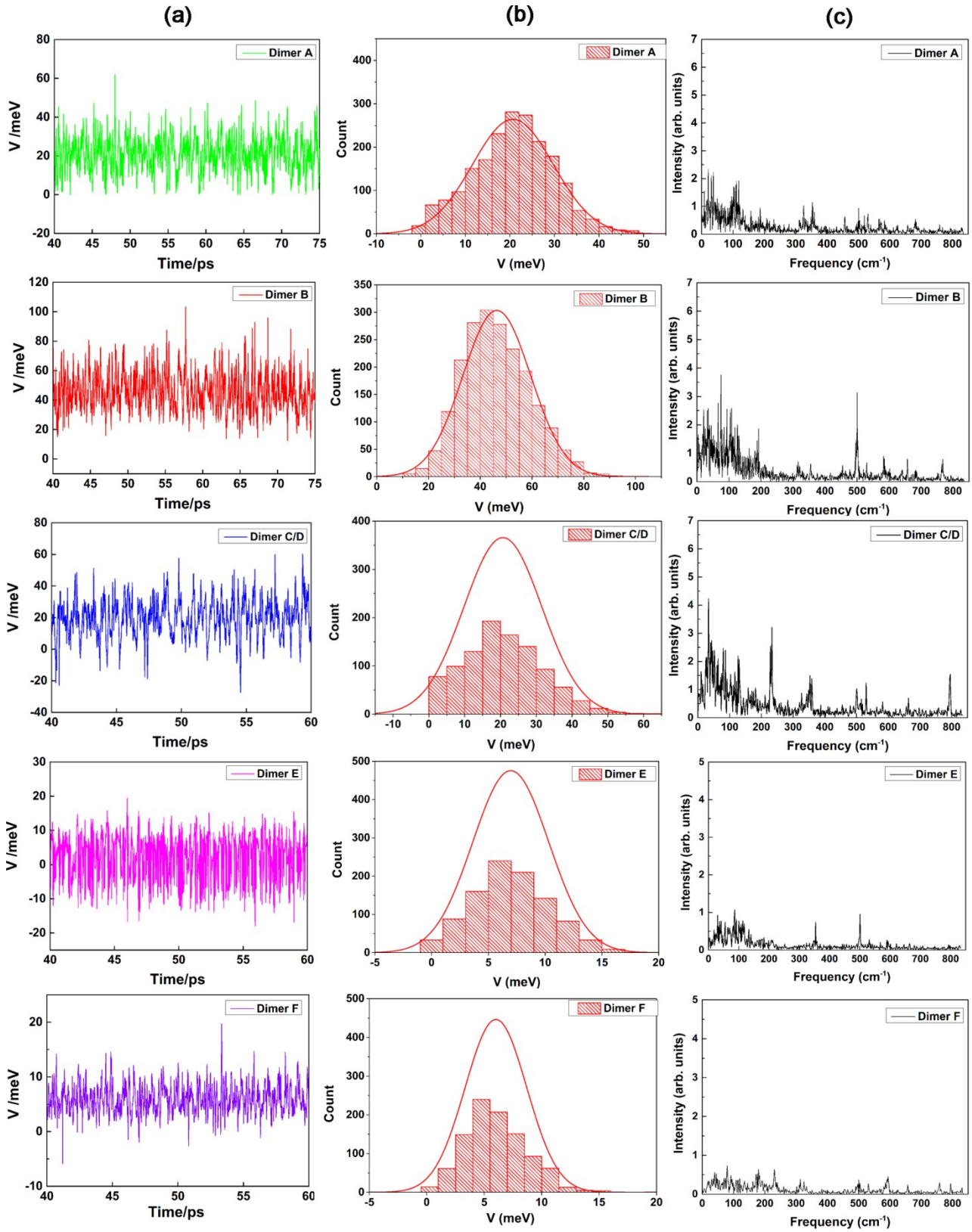


Figure S4. (a) Evolution of transfer integrals with sampling time at 300K, (b) gaussian fitting of the transfer integrals, and (c) the contributions of vibration modes to the transfer integral fluctuation for all the transport pathways in TCNQ crystal.

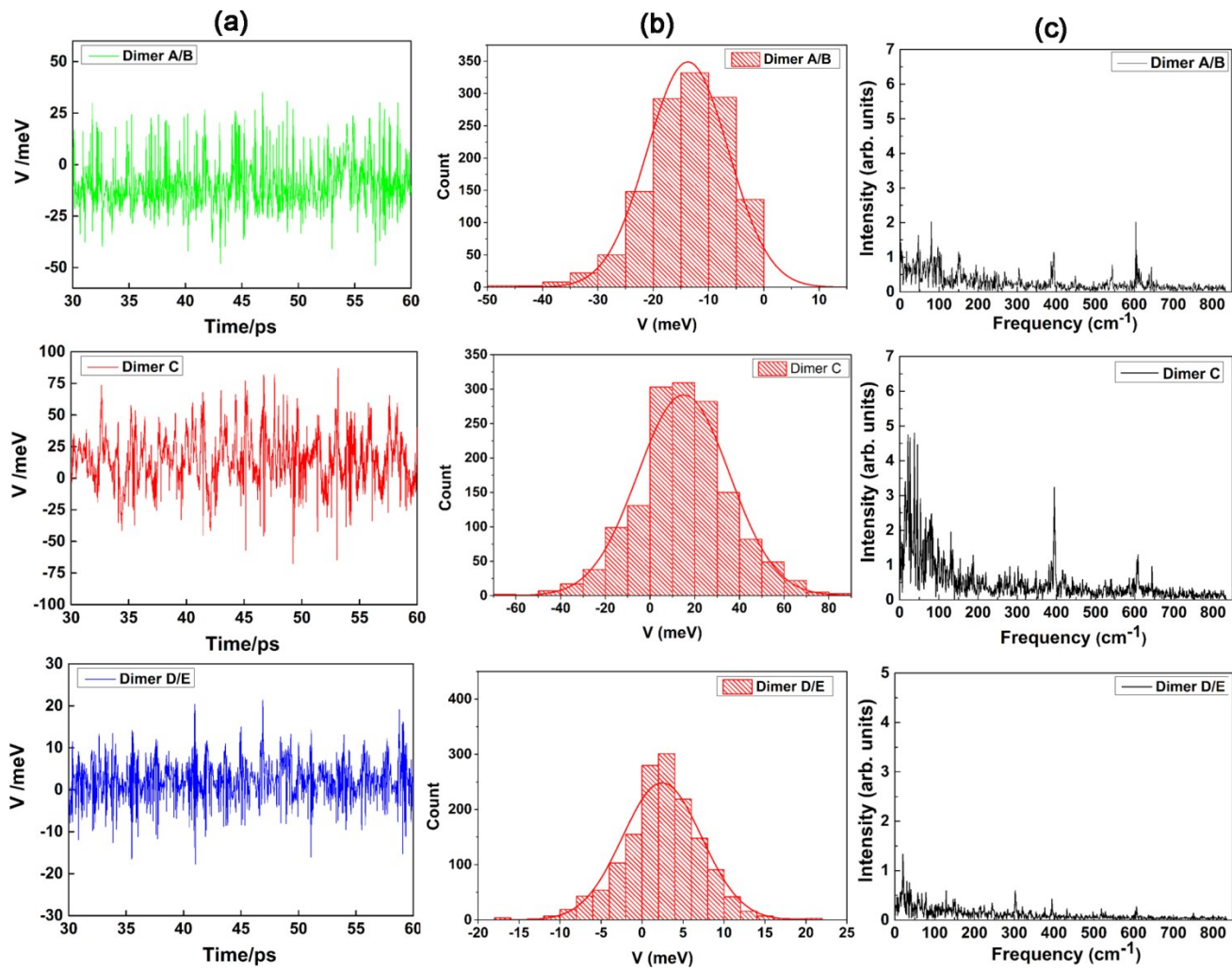
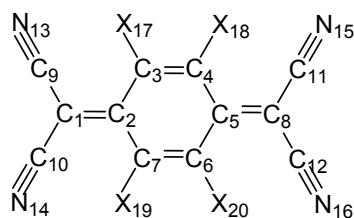


Figure S5. (a) Evolution of transfer integrals with sampling time at 300K, (b) gaussian fitting of the transfer integrals, and (c) the contributions of vibration modes to the transfer integral fluctuation for all the transport pathways in F_4 -TCNQ crystal.

Table S5. The natural charges for TCNQ, F₂-TCNQ and F₄-TCNQ molecules.



Number	Atom	TCNQ	F ₂ -TCNQ	F ₄ -TCNQ
		Natural Charge	Natural Charge	Natural Charge
1	C	-0.211	-0.090	-0.085
2	C	-0.014	-0.075	-0.148
3	C	-0.069	-0.272	0.460
4	C	-0.198	0.522	0.348
5	C	0.014	-0.097	-0.148
6	C	-0.157	-0.241	0.460
7	C	-0.159	0.450	0.348
8	C	-0.210	-0.091	-0.085
9	C	0.266	0.237	0.233
10	C	0.267	0.236	0.233
11	C	0.268	0.235	0.233
12	C	0.268	0.237	0.233
13	N	-0.252	-0.242	-0.218
14	N	-0.251	-0.228	-0.218
15	N	-0.251	-0.228	-0.218
16	N	-0.251	-0.242	-0.218
17	H/F	0.229	0.258	-0.300
18	H/F	0.237	-0.293	-0.295
19	H/F	0.237	-0.295	-0.295
20	H/F	0.237	0.258	-0.300

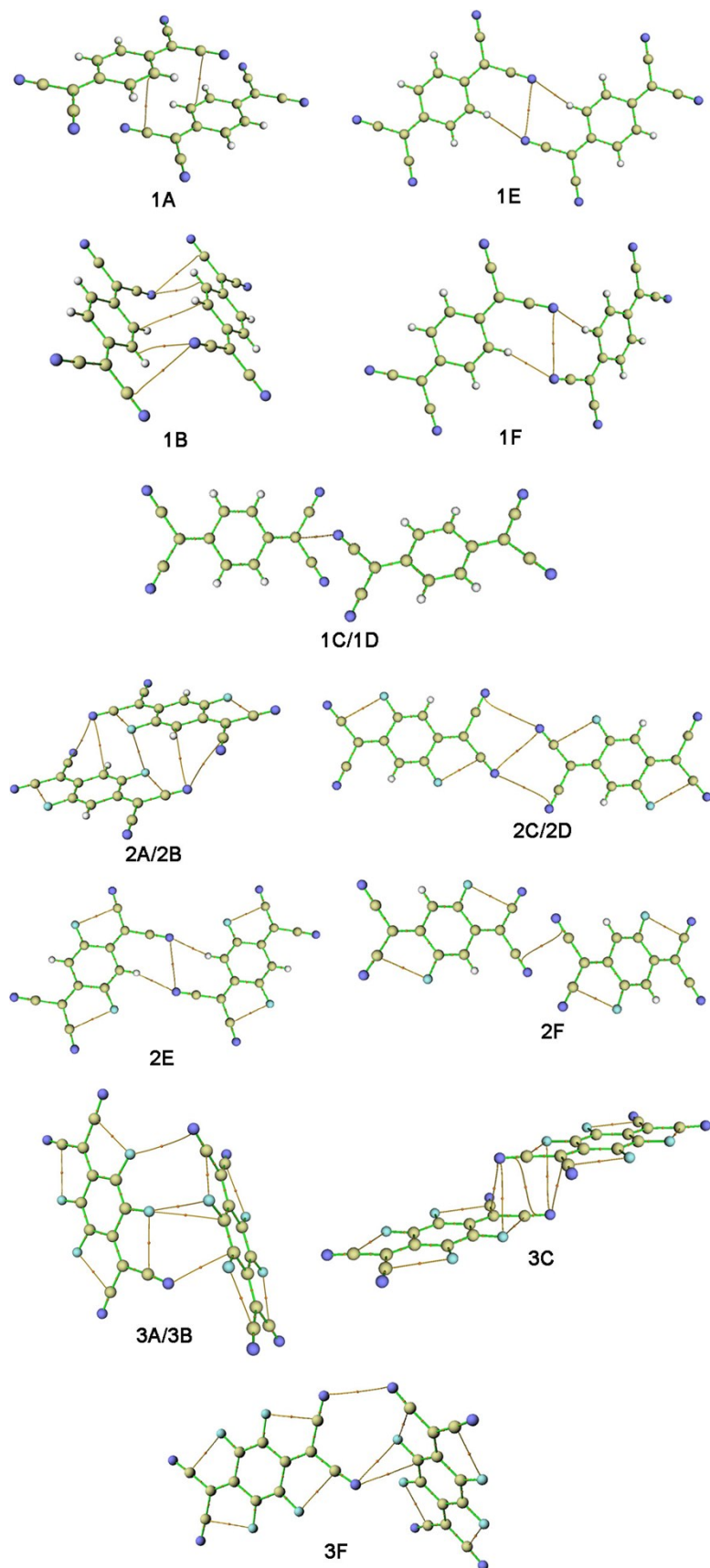


Figure S6 QTAIM electron density maps for various molecular pairs found in the crystals of TCNQ (1A-1F), F₂-TCNQ (2A-2F), and F₄-TCNQ (3A-3F).

Table S6. The topological parameters (electron density $\rho(r)$ and its Laplacian $\nabla^2\rho(r)$, kinetic energy density $G(r)$, potential energy density $V(r)$ and energy density $H(r)$) at the bond critical points (BCPs) obtained for intermolecular interactions involved various molecular pairs found in TCNQ crystal. Wave functions are calculated at B3LYP/6-31+G(d,p) level.

Molecular pairs	Main interactions	Distance/Å	$\rho(r)$	$\nabla^2\rho(r)$	$G(r)$	$V(r)$	$H(r)$
1A (5.641 Å)	C≡N...C	3.427	0.0051	0.0148	0.0030	-0.0023	0.0007
	C≡N...C	3.427	0.0051	0.0148	0.0030	-0.0023	0.0007
1B (5.641 Å)	C≡N...C	3.405	0.0042	0.0135	0.0027	-0.0021	0.0064
	C≡N...C	3.436	0.0043	0.0135	0.0027	-0.0020	0.0007
	C≡N...C	3.405	0.0042	0.0135	0.0027	-0.0021	0.0064
	C≡N...C	3.436	0.0043	0.0135	0.0027	-0.0020	0.0007
1C/1D (9.404 Å)	C≡N...C	3.153	0.0073	0.0238	0.0049	-0.0039	0.0010
1E (8.883 Å)	C≡N...H	2.511	0.0086	0.0296	0.0062	-0.0050	0.0012
	C≡N...H	2.511	0.0086	0.0296	0.0062	-0.0050	0.0012
1F (8.197 Å)	C≡N...H	2.544	0.0079	0.0270	0.0057	-0.0046	0.0011
	C≡N...H	2.544	0.0079	0.0270	0.0057	-0.0046	0.0011

Table S7. The topological parameters at BCPs between atoms in the intermolecular regions of various molecular pairs found in F₂-TCNQ crystal.

Molecular pair	Mian interactions	Distance/Å	$\rho(r)$	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)
2A/2B (5.896 Å)	C≡N...C	3.658	0.0025	0.0089	0.0017	-0.0012	0.0005
	C≡N...C	3.257	0.0058	0.0179	0.0037	-0.0029	0.0008
	C≡N...C	3.257	0.0058	0.0180	0.0037	-0.0029	0.0008
	C≡N...C	3.658	0.0026	0.0089	0.0017	-0.0012	0.0005
	F...F	3.001	0.0056	0.0306	0.0063	-0.0050	0.0013
2C/2D (9.314 Å)	C≡N...C≡N (dipole-dipole interaction)	3.275	0.0061	0.0206	0.0040	-0.0029	0.0011
2E (8.836 Å)	C≡N...H	2.461	0.0094	0.0323	0.0068	-0.0056	0.0012
	C≡N...H	2.461	0.0094	0.0323	0.0068	-0.0056	0.0012
2F (11.396 Å)	C≡N...N≡C	3.391	0.0046	0.0138	0.0030	-0.0025	0.0005
	C≡N...C≡N (dipole-dipole interaction)	3.472	0.0039	0.0123	0.0025	-0.0020	0.0005
	C≡N...C≡N (dipole-dipole interaction)	3.472	00039	0.0123	0.0025	-0.0020	0.0005

Table S8. The topological parameters at BCPs between atoms in the intermolecular regions of various molecular pairs found in F₄-TCNQ crystal.

Molecular pair	Mian interactions	Distance/Å	$\rho(r)$	$\nabla^2\rho(r)$	G(r)	V(r)	H(r)
3A/3B (6.145Å)	C≡N···F-C	3.094	0.0053	0.0223	0.0046	-0.0037	0.0009
	C≡N···C	2.937	0.0100	0.0343	0.0071	-0.0056	0.0015
	C-F···C	3.139	0.0044	0.0222	0.0043	-0.0031	0.0012
	C-F···F-C	2.972	0.0048	0.0277	0.0057	-0.0045	0.0012
3C (8.096Å)	C≡N···C≡N (dipole-dipole interaction)	3.327	0.0056	0.0182	0.0036	-0.0027	0.0009
	C≡N···C	3.414	0.0049	0.0152	0.0032	-0.0025	0.0007
	C≡N···C	3.414	0.0049	0.0152	0.0032	-0.0025	0.0007
	C≡N···F-C (dipole-dipole interaction)	3.288	0.0040	0.0174	0.0035	-0.0027	0.0008
	C≡N···F-C (dipole-dipole interaction)	3.288	0.0040	0.0174	0.0035	-0.0027	0.0008
	C≡N···F-C (dipole-dipole interaction)	3.288	0.0040	0.0174	0.0035	-0.0027	0.0008
3F (8.353Å)	C≡N···F-C (dipole-dipole interaction)	3.010	0.0070	0.0290	0.0062	-0.0052	0.0010
	C≡N···C	3.132	0.0067	0.0238	0.0048	-0.0037	0.0011
	C≡N···C≡N	3.284	0.0051	0.0159	0.0034	-0.0028	0.0006

Table S9. The total intermolecular interaction energy and energy decomposition analysis components for TCNQ molecular pairs extracted from its experimentally determined crystal calculated by SAPT(0)/jun-cc-pVDZ method. ($\Delta E_{\text{SAPT}(0)}$ is the total SAPT(0) interaction energy; E_{elect} , E_{exch} , E_{ind} , and E_{disp} are the electrostatic, exchange, induction, and dispersion contributions, respectively. All energy data are in kcal/mol. The values in parentheses indicate the centroid distances R.)

Molecular pairs	$\Delta E_{\text{SAPT}(0)}$	E_{elect}	E_{ind}	E_{disp}	E_{exch}
1A (5.641 Å)	-8.08	-2.41	-1.99	-10.78	7.10
1B (5.641 Å)	-5.04	-1.08	-1.64	-8.31	5.99
1C/1D (9.404 Å)	-4.82	-3.81	-0.80	-3.55	3.34
1E (8.883 Å)	-7.77	-6.95	-1.45	-3.54	4.18
1F (8.197 Å)	-6.44	-5.27	-1.26	-3.53	3.61

Table S10. The total intermolecular interaction energy and energy decomposition analysis components for F₂-TCNQ molecular pairs extracted from its crystal structure calculated by SAPT(0)/jun-cc-pVDZ method.

Molecular pairs	$\Delta E_{\text{SAPT}(0)}$	E_{elect}	E_{ind}	E_{disp}	E_{exch}
2A/2B (5.896 Å)	-9.04	-4.80	-2.15	-8.74	6.66
2C/2D (9.314 Å)	-5.73	-4.44	-1.01	-5.19	4.91
2E (8.836 Å)	-6.87	-6.54	-1.46	-3.89	5.03
2F (11.397 Å)	-1.51	-0.93	-0.39	-2.96	2.77

Table S11. The total intermolecular interaction energy and energy decomposition analysis components for F₄-TCNQ molecular pairs extracted from its crystal structure calculated by SAPT(0)/jun-cc-pVDZ method.

Molecular pairs	$\Delta E_{\text{SAPT}(0)}$	E_{elect}	E_{ind}	E_{disp}	E_{exch}
3A/3B (6.145 Å)	-6.35	-3.69	-2.05	-7.91	7.29
3C (8.096 Å)	-10.41	-7.22	-1.88	-6.85	5.54
3F (8.353 Å)	-4.69	-3.11	-1.00	-4.51	3.94