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Role of intermolecular charge delocalization and its dimensionality in efficient band-like electron transport in crystalline 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F_2-TCNQ)

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Supporting information

1. Transfer integrals within two calculation approaches

To verify our realization of the dimer projection (DIPRO) approach for the calculation of electron transfer integrals, *J*, the latter were also computed using energy-splitting-in-dimer (ESID) method, which is rigorous for symmetric dimers (i.e. in which the molecules are in equivalent positions). Table S1 collates the *J* values calculated using DIPRO and ESID approaches for symmetric dimers of TCNQ, F_2-TCNQ and F_4-TCNQ. The difference between the corresponding values obtained by the two methods does not exceed 7 meV (11%) for TCNQ, 4 meV (8%) for F_2-TCNQ and 8 meV (30%) for F_4-TCNQ. Reasonable coincidence of the values obtained by the two methods confirms the validity of the DIPRO-based approach for *J* calculation and its implementation in the current study.

Compound		TCNQ			F_2-TCNQ							F_4-TCNQ
Dimer type		*P1*	*P2*	*S*	*PL1*	*PL2*	*P1*	*P2*	*S1*	*L*	*S2*	*P*
J, meV	DIPRO	66	15	9	68	67	51	49	11	4	0	27
	ESID	59	12	1.5	64	63	46	45	11	4	0	19

Table S1. Electron transfer integrals *J* calculated using dimer projection (DIPRO) and energy-splitting-in-dimer (ESID) methods for F_2-TCNQ

2. Impact of basis set on transfer integrals and reorganization energy

2.1. Transfer integrals

Calculation of *J* in our current implementation of DIPRO method is not straightforward for large basis sets with diffuse functions; therefore, basis set 6-31g(d) was used for this task in the current study. The effect of basis set expansion on *J* values can be seen from Table S2 that presents the *J* values for the F_2-TCNQ crystal calculated using ESID method and different basis sets. The variation of *J* does not exceed 4 meV, and we conclude that the basis set used in this study, 6-31g(d), provides sufficiently accurate estimation of *J*.

Dimer type	*J, meV*			
	6-31g(d)	*6-31g(d,p)*	*6-31+g(d)*	*6-311+g(d,p)*
PL	62.5	62.5	61	61
P1,P2	45	45	45	46
S1	11	11	15	15
L	4	4	5	5
S2	0	0	1.5	0

Table S2. Values of electron transfer integrals for F_2-TCNQ crystal calculated using different basis sets.

2.2. Reorganization energy for isolated molecules

Basis set	*λ, meV*	
	TCNQ	*F_2-TCNQ*
6-31g	237	230
6-31g(d)	248	253
6-31g(d,p)	248	254
6-31+g(d)	250	258
6-31g+(d,p)	250	258
6-31g++(d,p)	250	258
6-311g(d,p)	257	265
6-311+g(d,p)	260	269
6-311g++(d,p)	260	269

Table S3. Reorganization energy for isolated molecules of TCNQ and F_2-TCNQ in different basis sets

Table S3 illustrates the effect of the basis set on the reorganization energy λ of isolated TCNQ and F_2-TCNQ molecules. The difference in λ between basis sets 6-31g and 6-311++g(dp) amounts ca 15%. This variation can not alter the conclusions of the current study.

2.3. Reorganization energy considering crystal environment

The effect of the basis set on λ values calculated considering crystal environment is illustrated in Table S4 for crystalline F_2-TCNQ. In both the 6-31g and 6-31+g(d) basis sets, λ in the selected PL dimer (see Chart 1 of the main text) amounts ca. 68% of that in single molecule. Similar variation of λ value for the two basis sets allow us to suggest that the qualitative results obtained in this study using relatively small 6-31g basis set are reliable.

Molecular system	*λ, meV*	
	6-31g	*6-31+g(d)*
Isolated molecule	230	258
Single molecule in crystal	240	263
Dimer	164	180

Table S4. Reorganization energy for F_2-TCNQ single molecule and dimer in different basis sets.