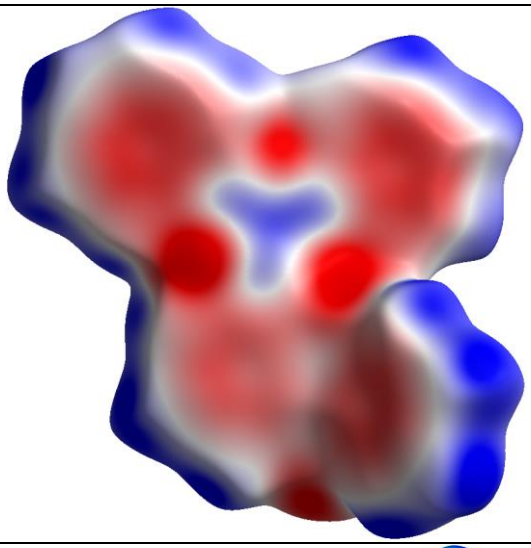
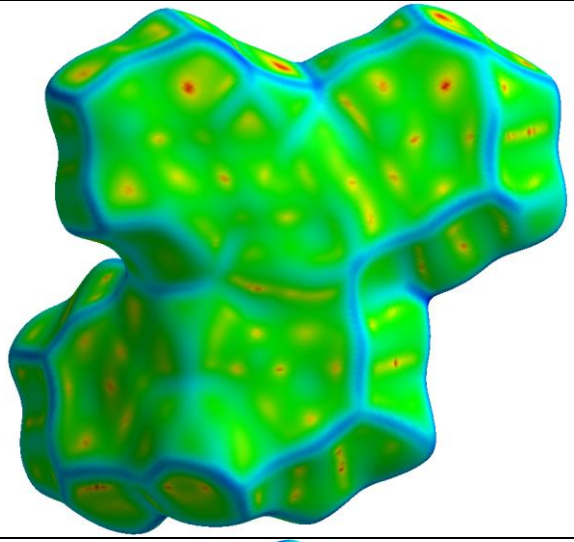
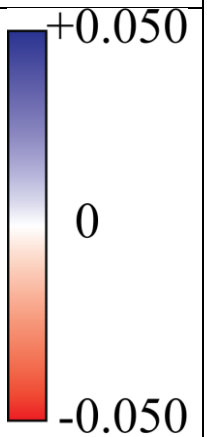
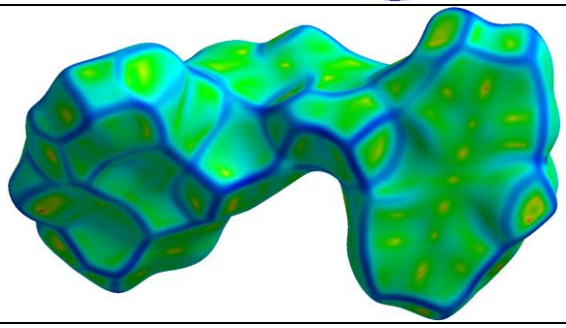
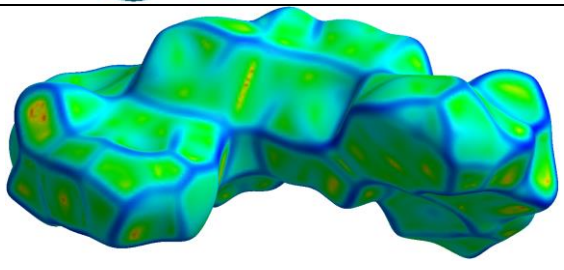
Supplementary Materials

Charge transport in organic semiconducting crystals exhibiting TADF: insight from quantum-chemical calculations

Andrey Yu. Sosorev[1,2]*, Dmitry I. Dominskiy[1,2], Nikita O. Dubinets[1,3]

1. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Science, Profsoyuznaya 70, Moscow 117393, Russia
2. Faculty of Physics and International Laser Center, Lomonosov Moscow State University, Leninskie Gory 1/62, Moscow 119991, Russia
3. Photochemistry Center, FSRC Crystallography and Photonics, Russian Academy of Sciences, Novatorov Str. 7A-1, Moscow, 119421, Russia

* Correspondence: sosorev@physics.msu.ru

	Front	Back	
a)			
b)			

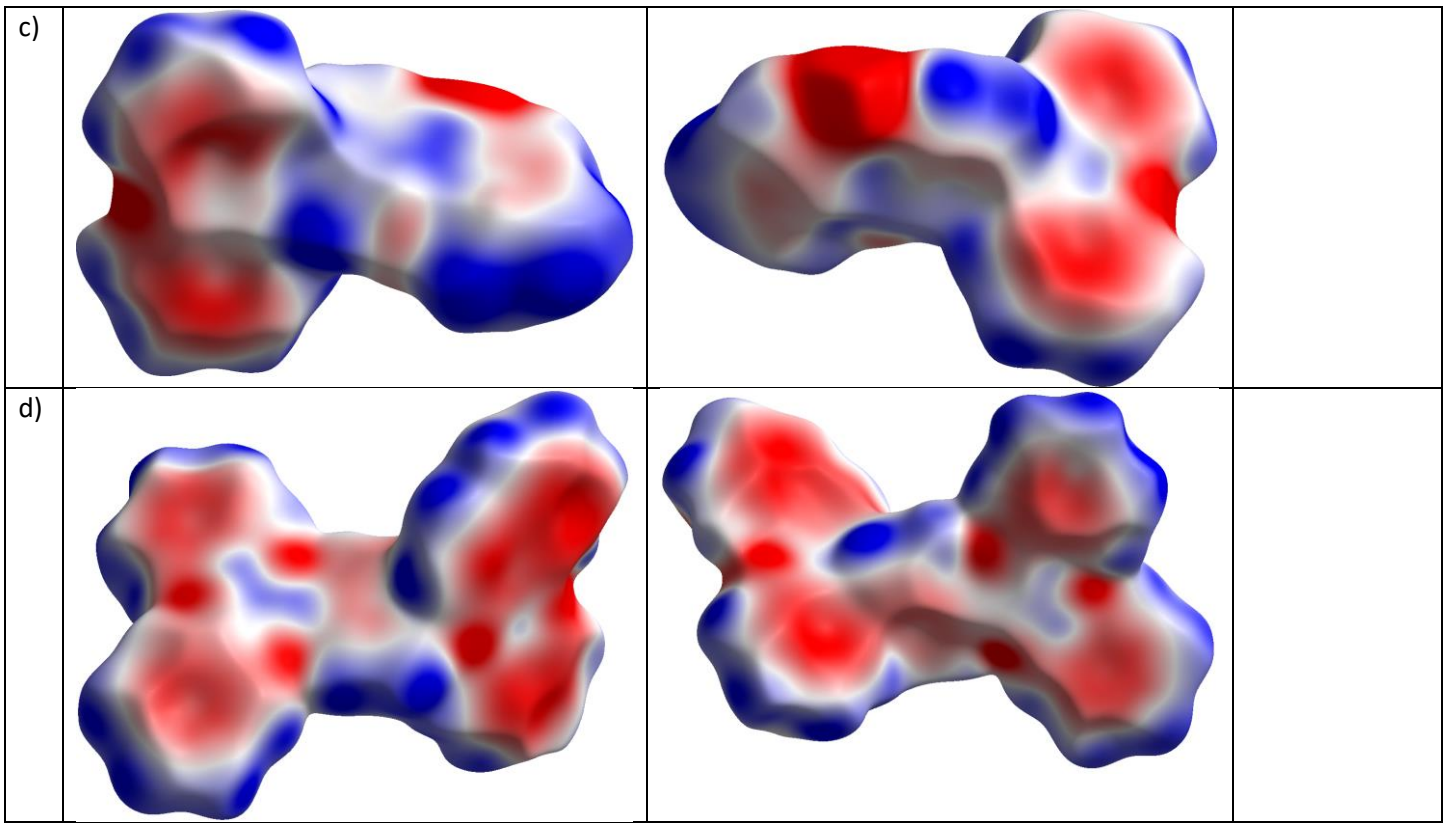


Figure S1. Hirshfeld surfaces (front and back of the molecules) mapped with electrostatic potential for crystalline oTE-DRZ (a), CPPD (b), PXZ-XO (c) and TRZ-c-BPXZ (d).

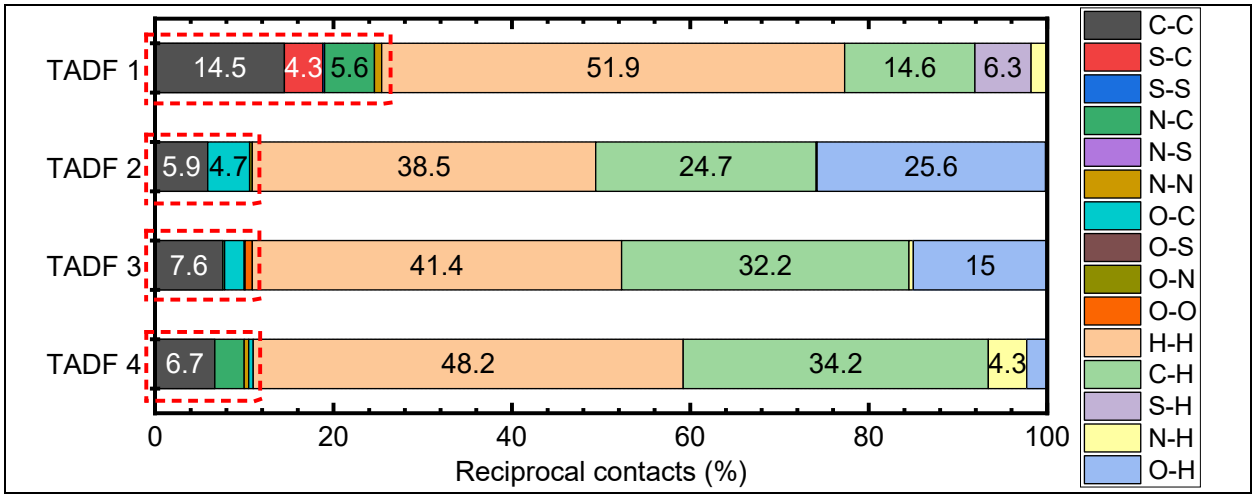


Figure S2. Distribution of reciprocal intermolecular contacts for oTE-DRZ, CPPD, PXZ-XO and TRZ-c-BPXZ crystals. “Conducting” contacts (*i.e.*, the contacts between the atoms bearing large HOMO and/or LUMO electron density) are highlighted with the red dashed frames.

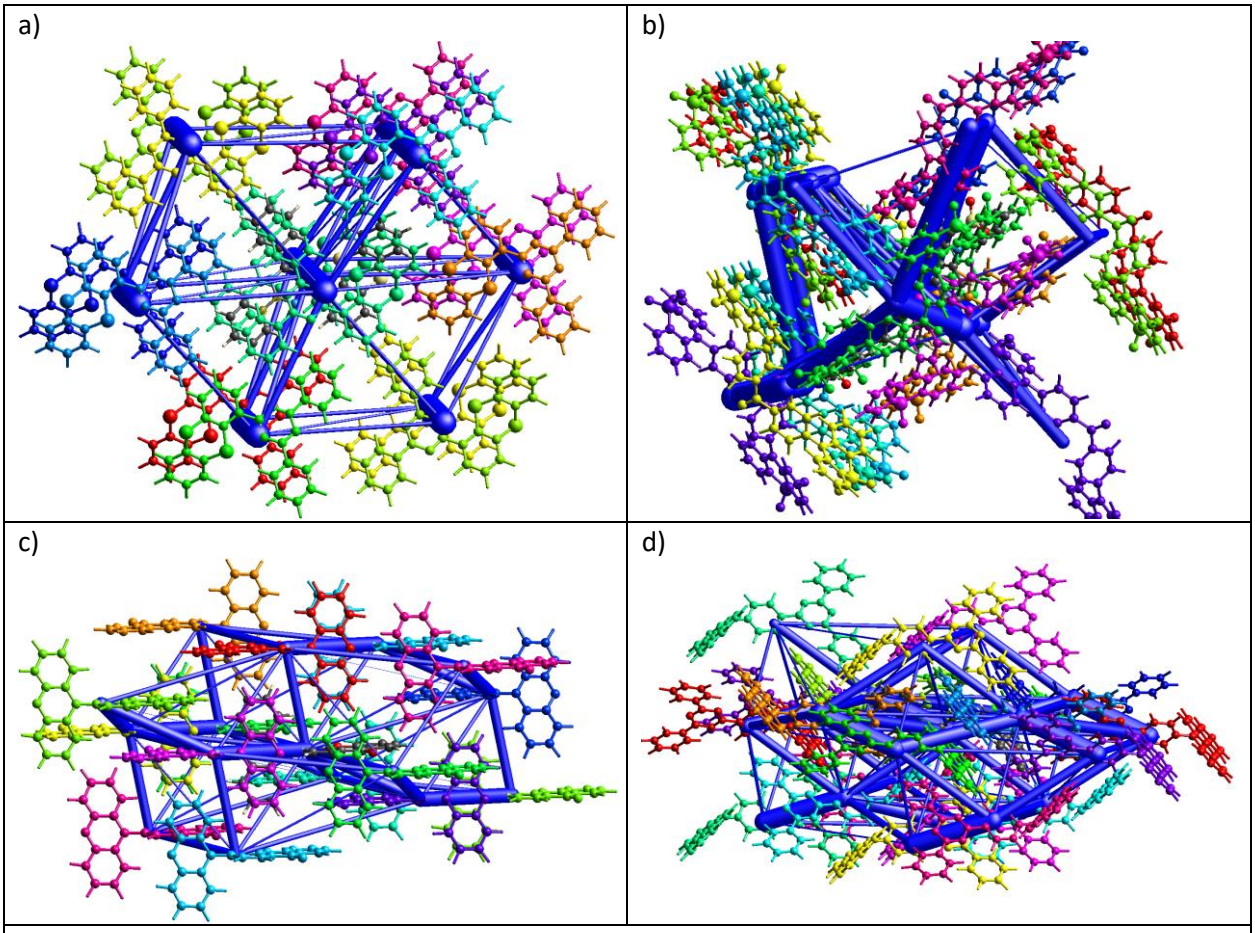


Figure S3. Graphical representation of total sum of interactions in oTE-DRZ (a), CPPD (b), PXZ-XO (c) and TRZ-c-BPXZ (d) crystals. The cylinders link molecular centroids, and their thickness is proportional to the magnitude of the energy; for clarity, pairwise energies with magnitudes less than 5 kJ mol^{-1} are omitted.

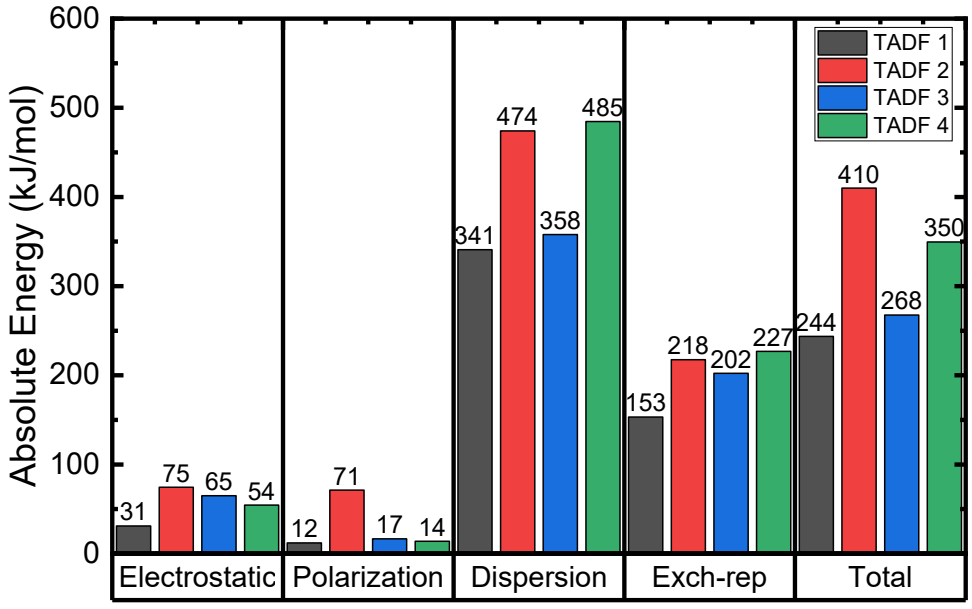


Figure S4. Distribution of sum of interaction energies (absolute values) in oTE-DRZ, CPPD, PXZ-CMO and TRZ-c-BPXZ for 3.8Å cluster.

Table S1. Different interaction energies of the molecular pairs for oTE-DRZ in kJ mol^{-1}: N is the number of pairs, R is the distance between the molecule centroids, E_ele is the classical electrostatic energy of interaction between monomer charge distributions, E_pol is the polarization energy estimated as a sum over atoms with terms of the kind $-\frac{1}{2}\alpha|\boldsymbol{F}|^2$, where the electric field F is computed at each atomic nucleus from the charge distribution of the other monomer and α are isotropic atomic polarizabilities, E_dis is Grimme's D2 dispersion correction summed over all intermolecular atom pairs, E_rep is the exchange–repulsion energy, obtained from the antisymmetric product of the monomer spin orbitals, and E_tot is the total energy.

	N	R (Å)	E_ele	E_pol	E_dis	E_rep	E_tot
	1	11.31	-6.8	-0.9	-32.0	17.1	-25.1
	0	13.81	1.4	-1.0	-17.2	0.0	-14.2
	1	12.44	-1.1	-0.4	-12.1	0.0	-11.9
	0	13.81	0.8	-0.3	-7.1	0.0	-5.6
	1	12.38	-0.5	-0.8	-21.6	0.0	-20.0
	1	3.98	-13.0	-5.3	-151.4	96.9	-89.7
	0	11.88	-1.5	-0.4	-10.5	5.6	-7.5
	0	14.10	-0.6	-0.2	-9.3	0.0	-8.9
	1	13.91	1.2	-0.6	-17.6	0.0	-14.5
	0	10.99	-6.5	-0.8	-30.1	19.9	-21.4
	0	13.50	-0.4	-0.6	-11.8	0.0	-11.1
	0	11.50	-4.0	-0.7	-20.2	13.7	-13.8

Table S2. Different interaction energies of the molecular pairs for CPPD in kJ mol^{-1}.

	N	R (Å)	E_ele	E_pol	E_dis	E_rep	E_tot
	2	15.95	1.7	-0.3	-3.3	0	-1.3
	1	6.80	-19.1	-13	-88.5	54	-73.5
	2	11.14	-5.5	-3.4	-29.1	21.2	-20.5
	2	12.99	18.3	-4	-27.1	0	-7.1
	2	8.62	-6.4	-4.6	-35.6	15	-31.8
	2	11.36	-25.5	-9.4	-40.1	33	-48.4
	2	16.81	-1	-0.5	-4.9	0	-5.8
	1	14.18	-3.9	-10.4	-66.5	0	-69.8
	2	14.46	-13.6	-3.2	-11.5	0	-26.8
	1	5.47	-7.6	-17.6	-151.9	94.4	-95.1
	1	18.53	-11.9	-4.9	-15.6	0	-29.8

Table S3. Different interaction energies of the molecular pairs for PXZ-XO in kJ mol^{-1}.

	N	R (Å)	E_ele	E_pol	E_dis	E_rep	E_tot
	1	7.27	-9.7	-1	-46.8	29	-33.8
	1	11.91	-1.6	-0.2	-8.1	2.8	-7.2
	1	12.61	0.3	-0.7	-22.3	0	-19.6

	2	16.27	0.2	-0.1	-2	0	-1.6
	2	7.69	-11.5	-3.6	-30.4	21.2	-28.1
	1	6.51	-15.9	-3	-61.9	43.7	-45.9
	2	9.84	-2.7	-0.3	-20.6	11.6	-13.9
	1	14.58	-3.3	-0.4	-15.3	0	-17.1
	1	8.74	-7.4	-2.7	-66.9	46.6	-39.4
	1	8.52	-13.4	-3.5	-74.9	47.3	-52.7
	2	12.38	0	-1.1	-8.7	0	-8.3

Table S4. Different interaction energies of the molecular pairs for TRZ-c-BPXZ in kJ mol^{-1}.

	N	R (Å)	E_ele	E_pol	E_dis	E_rep	E_tot
	2	16.52	0.2	-0.7	-19.1	0	-16.9
	1	14.46	3.3	-1.4	-58.7	0	-48.6
	2	11.76	-3.5	-0.7	-17.8	10.3	-13.4
	1	7.12	-12.1	-2.1	-119.2	63.5	-79
	2	11.28	-7.9	-0.9	-34.9	20.8	-26.6
	2	16.85	0.8	-0.2	-5.9	0	-4.5
	2	10.02	-11.1	-1.6	-57.4	37.7	-39.6
	1	9.12	-7	-1.4	-44.5	28.1	-29.7
	1	10.71	-11.6	-3.6	-86.1	45.9	-61.5
	2	14.51	1.2	-0.3	-9.9	0	-7.5
	2	8.65	-4.4	-0.6	-21.9	16.7	-13.9
	2	11.52	-2.3	-0.4	-9.3	3.9	-8.4

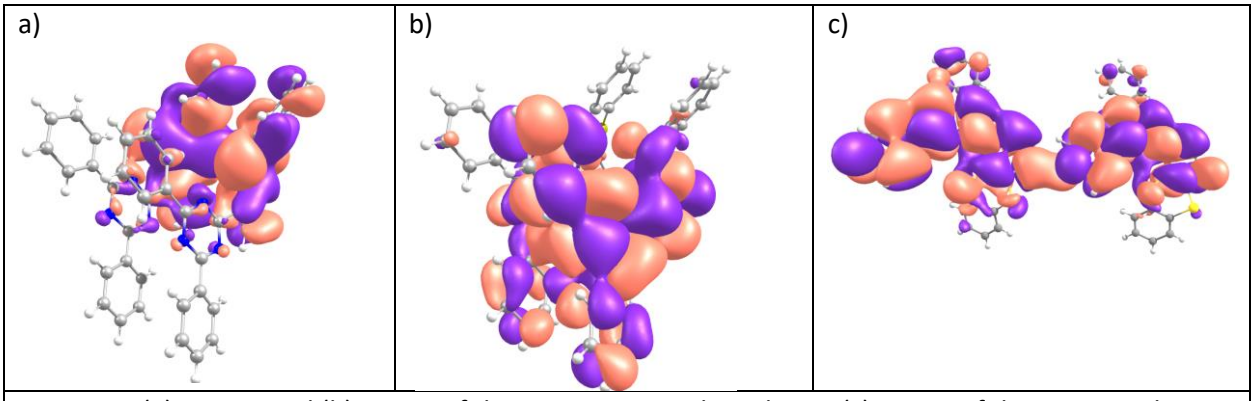


Figure S5. (a) HOMO and (b) LUMO of the oTE-DRZ π-stacking dimer. (c) LUMO of the oTE-DRZ dimer showing the largest electron-transfer integral.

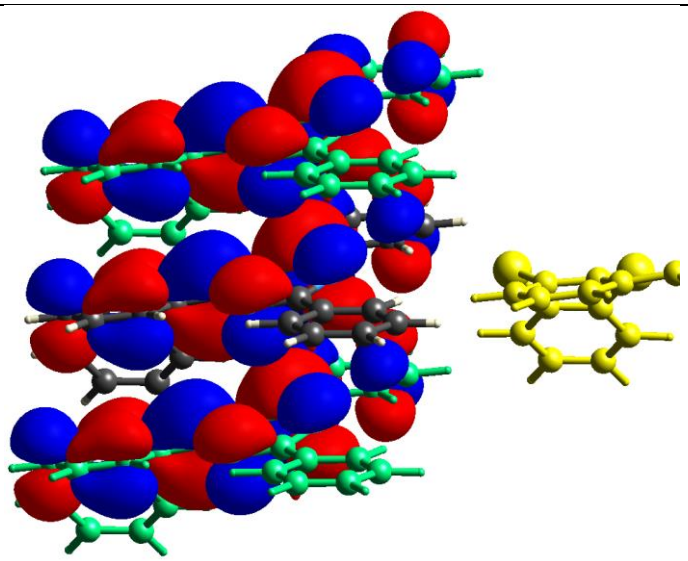


Figure S6. LUMO of the oTE-DRZ π-stack. Wavefunction phase mismatch between adjacent molecules is clearly observed.