Electronic supplementary information (ESI) for

Crystal packing of TCNQ anion π-radicals governed by intermolecular covalent π–π bonding: DFT calculations and statistical analysis of crystal structures[†]

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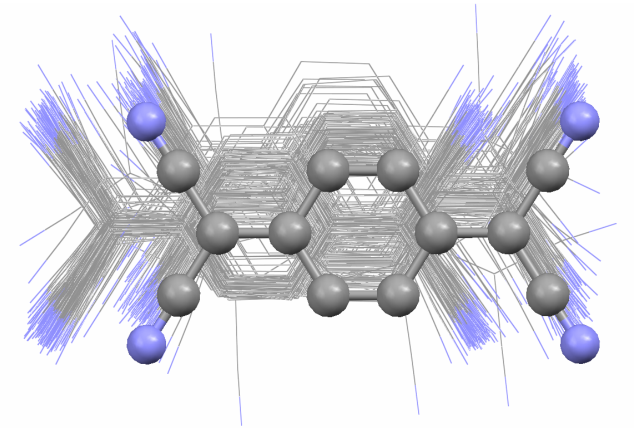

CSD scatterplot showing the distribution of TCNQ fragments (wireframe) with respect to the central group (ball and stick).

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Table S1 Coordinates of TCNQ anion radical of symmetry D_{2h} optimized with UB3LYP/6-31G*

Atom	x	y	z
C	0.000000	0.000000	1.434497
C	0.000000	1.213473	0.687556
C	0.000000	1.213473	-0.687556
C	0.000000	0.000000	-1.434497
C	0.000000	-1.213473	-0.687556
C	0.000000	-1.213473	0.687556
C	0.000000	0.000000	2.867097
C	0.000000	-1.205815	3.608658
C	0.000000	1.205815	3.608658
C	0.000000	0.000000	-2.867097
C	0.000000	-1.205815	-3.608658
C	0.000000	1.205815	-3.608658
N	0.000000	-2.209824	4.210107
N	0.000000	2.209824	4.210107
N	0.000000	-2.209824	-4.210107
N	0.000000	2.209824	-4.210107
H	0.000000	2.158422	1.223597
H	0.000000	2.158422	-1.223597
H	0.000000	-2.158422	1.223597
H	0.000000	-2.158422	-1.223597

Table S2 Coordinates of TCNQ anion radical of symmetry D_{2h} optimized with ROB3LYP/6-31G*

Atom	x	y	z
C	0.000000	0.000000	1.434577
C	0.000000	1.213796	0.687452
C	0.000000	1.213796	-0.687452
C	0.000000	0.000000	-1.434577
C	0.000000	-1.213796	-0.687452
C	0.000000	-1.213796	0.687452
C	0.000000	0.000000	2.866393
C	0.000000	-1.206128	3.607674
C	0.000000	1.206128	3.607674
C	0.000000	0.000000	-2.866393
C	0.000000	-1.206128	-3.607674
C	0.000000	1.206128	-3.607674
N	0.000000	-2.210377	4.208521
N	0.000000	2.210377	4.208521
N	0.000000	-2.210377	-4.208521
N	0.000000	2.210377	-4.208521
H	0.000000	2.158554	1.223784
H	0.000000	2.158554	-1.223784
H	0.000000	-2.158554	1.223784
H	0.000000	-2.158554	-1.223784

Table S3 Bond lengths of neutral and anionic TCNQ monomers from X-ray structures and DFT optimizations (From $q = 0$ to 1, the bond lengths of C1-C2 and C7-C9 shorten and the bond lengths of C1-C7 and C2-C3 lengthen in accordance with the bonding and antibonding characteristics of the LUMO of TCNQ shown in Fig. 5)

System	TCNQ		$TCNQ^{-}$		
Theory[a]	RB3LYP	Exp.[b]	ROB3LYP	UB3LYP	Exp.[c]
C1-C2[d]	1.447	1.448	1.425	1.425	1.423
C2-C3	1.356	1.346	1.375	1.375	1.373
C1-C7	1.390	1.374	1.432	1.433	1.420
C7-C9	1.427	1.441	1.416	1.416	1.416
C9-N2	1.165	1.140	1.170	1.170	1.153

[a] Basis set is 6-31G*.

[b] Average values from ref. S1 (TCNQ).

[c] Average values from ref. S2 ($Rb^{+}TCNQ^{-}$).

[d] For atomic numberings, see Fig. 2.

Table S4 Structures of TCNQ σ-dimers found in CSD with bond length r, calculated longitudinal offset L, and transversal offset T

Refcode	Compound [a]	r (Å) [b]	L [c]	T [c]	Ref.
CABKEV	$[Cu(DMP)_2]_2[TCNQ]_2$	1.630(13)	6.38	0.40	S3
EPZTCD	$[EtP]_2[TCNQ]_2$	1.631(5)	6.41	0.14	S4
FIWPAD	$[Fe(phen)_3][TCNQ]_2$	1.645(7)	6.42	0.18	S5
GAXYEJ	$[TDAC]_2[TCNQ]_2$	1.626(6)	6.53	0.16	S6
OBAPUC	$Zn[TCNQ]_2[MeOH]_2$	1.641(5)	6.37	0.10	S7
RECTAU	$Mn[TCNQ]_2[MeOH]_4$	1.659(10)	6.26	0.08	S8
RECTAU01 [d]	$Mn[TCNQ]_2[MeOH]_4$	1.659(10)	6.26	0.08	S7
RECTEY	$Mn[TCNQ]_2[MeOH]_2$	1.635(10)	6.34	0.08	S8
RECTEY01	$Mn[TCNQ]_2[MeOH]_2$	1.635(10)	6.34	0.08	S7
TCQDPT	$[Pt(2,2'\text{-dipy})_2][TCNQ]_2$	1.65(2)	6.46	0.09	S9
WARVEQ	$[Mn(TMesP)]_2[TCNQ]_2[PhCl]_4$	1.61(1)	6.36	0.12	S10

[a] See the references for the abbreviations for some of the electron donors.

[b] See Chart 3 (cf. $[TCNE]_2^{2-}$ σ-dimer in Chart 2).

[c] Values were calculated similar to the π-dimers shown in Fig. 2.

[d] Possibly a duplicate deposition in the CSD.

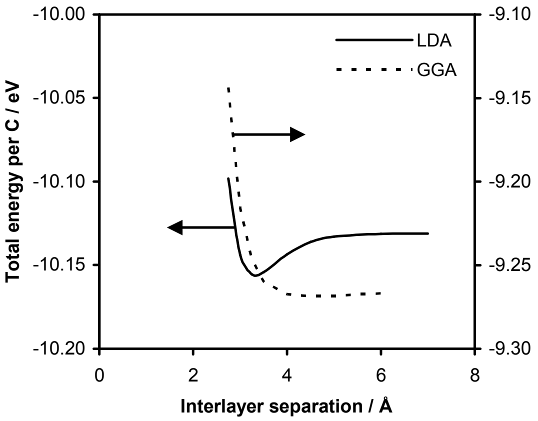

Fig. S1 Potential energy curves of hexagonal graphite with ABAB packing as a function of interlayer separation calculated with LDA and PW91, showing a minimum at 3.25Å for LDA and almost no minimum for PW91. The unit cell constant ***c*** is twice the interlayer separation and its experimental value is 6.71 Å. The calculations were performed using the Vienna ab initio simulation package (VASP)[S11] with Vanderbilt-type[S12] ultrasoft pseudopotentials[S13] using a 42x42x14 ***k***-point mesh. The kinetic energy cutoff on the wave function expansion was 358.2 eV. The interlayer separation (or vector ***c***) is fixed in each calculation and only the in-plane vectors ***a*** and ***b*** are allowed to relax.

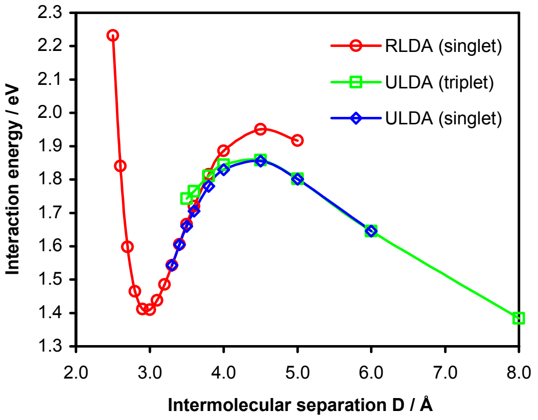

Fig. S2 Intermolecular interaction between two TCNQ anion radicals in the $[TCNQ]_2^{2-}$ π-dimers as a function of D with longitudinal and transversal offsets fixed at L = 2.2 Å and T = 0 Å calculated with RLDA/6-31G* (closed-shell singlet), ULDA (open-shell triplet), and ULDA (open-shell singlet).

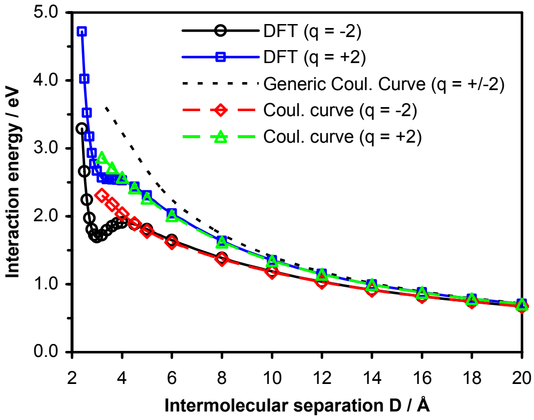

Fig. S3 Intermolecular interaction with BSSE correction between two TCNQ radicals in the $[\mathrm{TCNQ}]_2^{2-}$ and $[\mathrm{TCNQ}]_2^{2+}$ π-dimers as a function of D with longitudinal and transversal offsets fixed at L = 2.2 Å and T = 0 Å. The generic coulombic curve was calculated between two point charges each having q = −1 with the same distances *r* as the DIST1 values of the $[\mathrm{TCNQ}]_2^{2-}$ π-dimers. The specific coulombic repulsion energies were calculated following eqn (10) by $E_{\mathrm{int}} - E_{\mathrm{bond}} - E_{\mathrm{vdW}}$ where E_{vdW} is the interaction energy also with BSSE correction for the neutral $[\mathrm{TCNQ}]_2$ π-dimers.

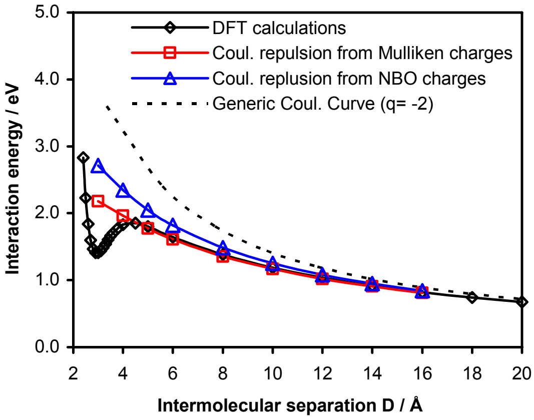

Fig. S4 Intermolecular interaction between two TCNQ anion radicals in the $[\mathrm{TCNQ}]_2^{2-}$ π-dimers as a function of D with L = 2.2 Å and T = 0 Å. The specific Coulombic repulsion energies were calculated using the Mulliken and natural atomic charges. The Coulombic energies from natural atomic charges are slightly higher than those from Mulliken charges. Nevertheless, its curve almost converges with the interaction energy curve at ca. 8 Å while the generic Coulombic curve converges at ca. 14 Å.

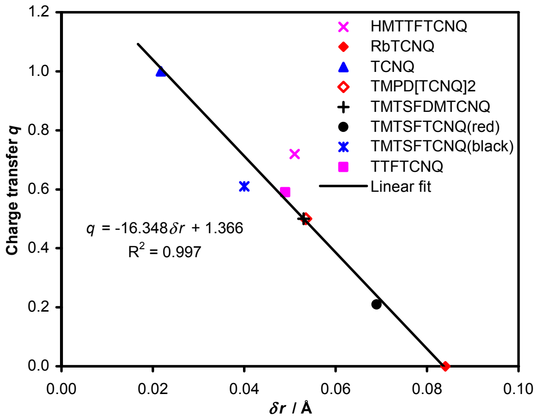

Fig. S5 Correlation diagram between charge transfer *q* and bond length alternation δr for TCNQ salts with experimentally known degree of charge transfer (charge transfer taken from ref. 38). The linear fit is then used for the estimate of charge transfer in the text.

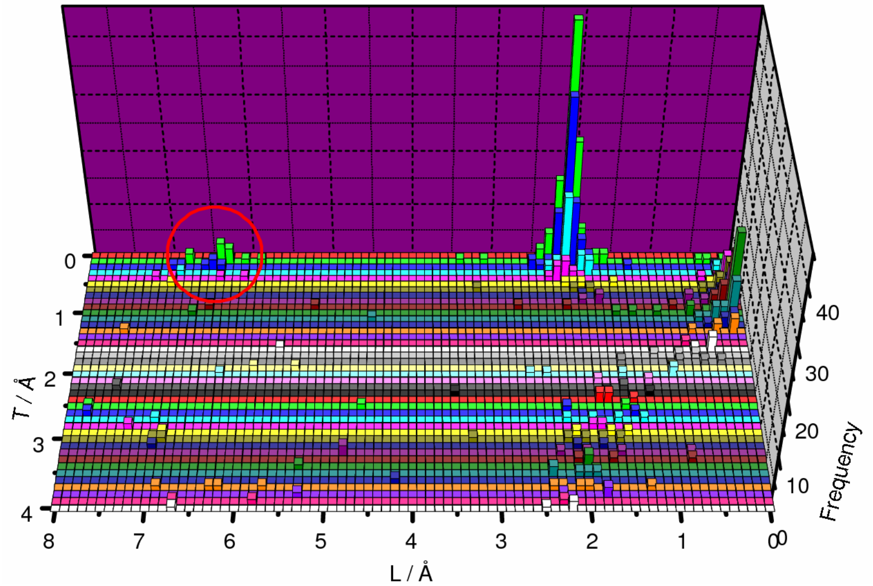

Fig. S6 3D histogram of TCNQ dimer packing as a function of the longitudinal offset L and the transversal offset T in Å, with the structures in Table S4 included which are highlighted by the red circle.

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